

PHASE CHANGE, MIXTURES, AND ENGINES

In this chapter, I will go more deeply into some phenomena having to do with phase change and mixtures of gases such as moist air. These will lead to important applications in engineering and the natural sciences. First, there will be a description of phase change that makes use of concepts developed in the previous chapters. Then I turn to mixtures of two phase fluids such as moist air which will allow me to briefly discuss evaporation. Simple models of vapor power and refrigeration cycles will conclude this chapter.

15.1 PHASE CHANGES IN SIMPLE FLUIDS

In Chapter 5, phase change of simple fluids was discussed from the viewpoint of the entropy needed to melt or vaporize a substance. Then, in Chapter 6, the phenomenon was described as a chemical reaction. This led to explanations of the change of melting or boiling points, and vapor pressure. The chemical viewpoint prepares us for the discussion of the entropy necessary for phase changes, vapor pressure and Clapeyron's law, and property tables.

15.1.1 A Description of Phase Changes

Here, we will describe in more concrete terms what happens to a fluid as a consequence of fusion, vaporization, or sublimation. So that we will not always have to mention all three processes, we will usually choose one of them as an example. We will see how much entropy and energy are involved in a phase change, and we will discover that there exist clear relations between the temperature and the pressure at the transition. In Chapter 4 and 5, we described the melting or the vaporization of a body using the TS diagram of the process, a tool which we will use again. We will begin by describing the processes of vaporization and condensation.

Vaporization of water. For the sake of argument, consider 1 kg of water being heated from 0°C at a constant pressure of 1 bar (Fig. 15.1). For water being heated, entropy and temperature rise from values of zero along the section of the curve at the bottom left (for entropy, this is an arbitrary choice). During this phase, water is said to be a *compressed (subcooled) liquid*. Since water is nearly incompressible, the relation is approximated by the one derived in Chapter 4 (Equ.(4.42)):

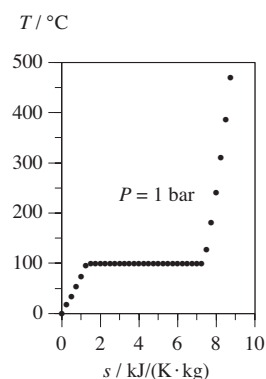


Figure 15.1: For 1 kg of water being heated at constant pressure of 1.0 bar, the temperature rises as a function of the entropy content. The horizontal section of the curve corresponds to the phase during which vaporization takes place: addition of entropy does not change the temperature of the fluid.

$$s(T) = s(T_0) + c_p \ln\left(\frac{T}{T_0}\right) \quad (15.1)$$

This agrees well with what can be read from Fig. 15.1. (Remember that c_p for water is about $4200 \text{ J}/(\text{kg} \cdot \text{K})$.) At a temperature of 100°C , the water begins to boil. Just before the onset of boiling, the fluid is said to be a *saturated liquid*. While the entropy of the fluid increases, the temperature stays constant: the curve cuts horizontally through the TS diagram at the temperature of vaporization. During this part of the process, the fluid is a *mixture of liquid and vapor*. Finally, when all the water has been turned into steam, the temperature of the vapor begins to rise again as its entropy increases. Again, there is a name for the fluid just after the point when all of it has turned into gas: it is called a *saturated vapor*. When heated, pure vapor (without any liquid left) is said to be *superheated water vapor*. Equ.(15.1) can be accepted as an approximation for the actual relation between temperature and entropy for the gas as well, if we take steam as an ideal gas having a constant temperature coefficient of enthalpy, see Chapter 5. (According to Fig. 15.1, the average value of c_p between 100°C and 200°C is around $2000 \text{ J}/(\text{kg} \cdot \text{K})$.)

Amount of substance, entropy, and energy. Let us take a closer look at the transition and the balance of entropy and energy (Fig. 15.2). Consider the pure liquid at the boiling point. Entropy is added, and a certain amount of the liquid is transformed into vapor. Looked at from the viewpoint of a chemical reaction, we may say that only one substance is involved on either side of the reaction equation



As a consequence, if the change of amount of substance of species A is Δn , then the corresponding change for B is $-\Delta n$:

$$\Delta n_l = -\Delta n_g \quad (15.2)$$

The subscripts l and g indicate the liquid and vapor (gaseous) phases, respectively. In terms of the change of the amount of substance of the vapor, the entropy necessary for vaporization can be written as follows:

$$S_{e,v} = \bar{l}_v \Delta n_g \quad (15.3)$$

Observation tells us that vaporization at constant pressure and temperature proceeds reversibly. This means that the entropy added to the liquid phase will be present in the vapor phase (Fig. 15.3). The *latent entropy* l of the phase change can therefore be expressed in terms of the entropies of the liquid and the gas:

$$\bar{l}_v = \bar{s}_g - \bar{s}_l \quad (15.4)$$

The phase change is also described in terms of the energy exchanged (see Fig. 15.2). Since the process takes place at constant temperature, the energy added for vaporization is the product of T_v and $S_{e,v}$ as expressed by Equ.(15.3). If we remember that the phase change also takes place at constant pressure, we can conclude that the energy added in heating is equal to the change of enthalpy of the fluid, see Chapter 5. Part of the energy is used to raise the internal energy, while the rest is emitted because of the

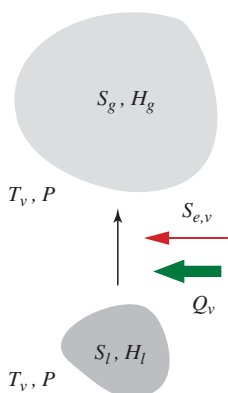


Figure 15.2: A certain amount of a liquid vaporizes. The entropy added remains in the body, while part of the added energy goes toward expansion. The added energy is equal to the change of enthalpy of the fluid body.

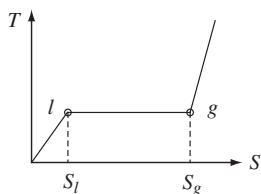


Figure 15.3: The entropy of vaporization can be read from the TS diagram, where the value corresponds to the length of the horizontal section of the curve. Points l and g denote the states of saturated liquid and of saturated vapor (gas).

expansion of the fluid. In summary, the change of entropy and the change of enthalpy (the latent enthalpy of vaporization) are related by

$$\bar{h}_g - \bar{h}_l = T_v (\bar{s}_g - \bar{s}_l) \quad (15.5)$$

Naturally, these relations can also be expressed on the basis of mass rather than amount of substance. We simply introduce the specific entropy of vaporization l_v and relate it to the difference of the specific entropies of the fluid in the liquid and the vapor phases. Then, in Equ.(15.5), we have the specific enthalpy and the specific entropy. The latent enthalpy of vaporization is sometimes abbreviated by Δh_v .

Vaporization at different pressures. From experience we know that water boils at different temperatures depending upon the pressure of the fluid. If the pressure is lower than 1 bar, the boiling point is also lower. Since the change in pressure hardly affects the properties of liquid water, we expect a TS diagram of the process of heating to start off just as in the lower left of the curve in Fig. 15.1. Then, however, the curve must break off at an earlier point and cut across the diagram horizontally. Measurements show that more entropy is needed to vaporize the same amount of water at lower pressure. Finally, when all the water has turned into steam, the temperature continues to climb again. For higher pressures, the changes with respect to the case of 1 bar are just the opposite. If the TS curves for different values of the pressure are drawn in the same diagram, we get the result shown in Fig. 15.4. The amount of energy necessary for vaporization depends not only upon the amount of entropy needed, but also upon the temperature of vaporization. It turns out the amount of energy necessary for vaporization decreases with increasing pressure.

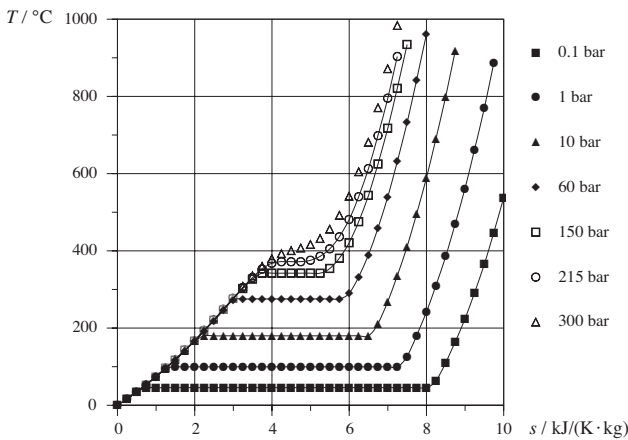
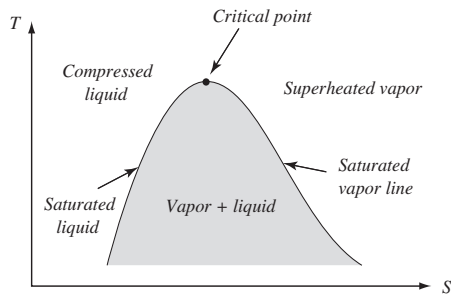


Figure 15.4: TS diagram for 1 kg of water heated from 0°C at constant pressure. The curves are for different values of pressure, ranging from 0.1 bar to 300 bar. The last set of points shows that when the pressure is larger than the critical pressure of 220 bar, the vapor does not condense any more. The values were computed using the Steam-NBS function implemented in the program EES (Klein et.al, 1991).

There are some interesting points to note. The horizontal sections of the TS curves, i.e., those parts which display the process of vaporization, form a bell-shaped area on the TS diagram (Fig. 15.5). The diagram can be divided into three sections, one on the left of the bell for the *compressed liquid phase*; one to the right, for the *superheated vapor*; and the bell area itself, where *mixtures of liquid and vapor* are present. The liquid phase basically occupies only a very thin strip along the saturated liquid line; this is because the properties of liquid water do not depend strongly upon pressure. Only for

very large pressures, of the order of hundreds or thousands of bar, do the properties of water differ considerably from the saturated state. The curve bounding the bell is divided into two parts; the left denotes the states of *saturated liquid* (pure liquid just at the verge of vaporization), and the right shows the states of *saturated vapor* (pure vapor on the verge of condensation). The two sections meet at the top of the bell, at a point called the *critical point*. If you have water vapor at pressures above the critical pressure of 220.9 bar, and you cool the vapor at constant pressure, it will no longer condense. Rather, as you can see in Fig. 15.4, the temperature will pass above the critical temperature of 374.14°C for values of the specific entropy of 4.43 J/(K·kg).

Figure 15.5: The line for saturated fluid (liquid and vapor) is shown in the TS diagram. The dome shaped area below the line is occupied by the mixed phase of liquid and vapor. The line separates this area from those of the compressed liquid and the superheated steam.



The pressure-temperature relation for boiling. Obviously, there is a relation between the boiling point, i.e., the temperature of vaporization, and the pressure at which the transition takes place. As Fig. 15.4 demonstrates, the higher the pressure, the higher the temperature. Such a relation is rather different from what we know about liquids or gases. With incompressible liquids, the properties depend only upon the temperature, and the pressure does not come into play. For gases, on the other hand, two independent properties define the temperature; one variable, such as the pressure, is not enough. For this reason, the relation between temperature and pressure at vaporization is remarkable. A typical pressure-temperature curve for a fluid appears in Fig. 15.6. Note that the line has a beginning and an end. The end we already know: it is the critical point of the fluid. The beginning of the line, however, will be understood shortly, when we transfer our description to the other two phase transitions as well. The beginning point is called the *triple point* of the substance.

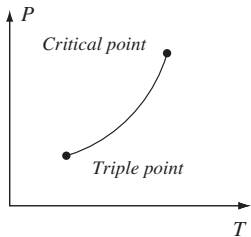


Figure 15.6: At vaporization, pressure and temperature of the fluid are directly related. P is called the vapor pressure at T .

Pressure-temperature relations for all three phase transitions. Most of the observations made about vaporization can be transferred to melting and sublimation (the direct transition between solid and vapor). Specific amounts of entropy are needed for these transformations (or are emitted for the reverse processes); the energy required is related to this quantity by the temperature of the phase transitions. While the process runs at constant pressure, the temperature stays constant. In each case, the pressure is only dependent upon the temperature during the change.

Take the case of water freezing or ice melting. Even though it is harder to observe, changes of pressure affect the melting point; the reason for the difficulty lies in the fact that the pressure-temperature curve for melting is very steep (Fig. 15.7). On the other hand, this effect leads to the phenomenon of freezing water being able to split rocks: water freezing at temperatures only slightly below 0°C develops a tremendous pressure. Having observed this, we have to conclude that the pressure-temperature relation for melting has a negative slope, unlike what we know of the vaporization of water,

and, in fact, just about unlike anything else known in nature. Water expands upon freezing, while most other substances contract.

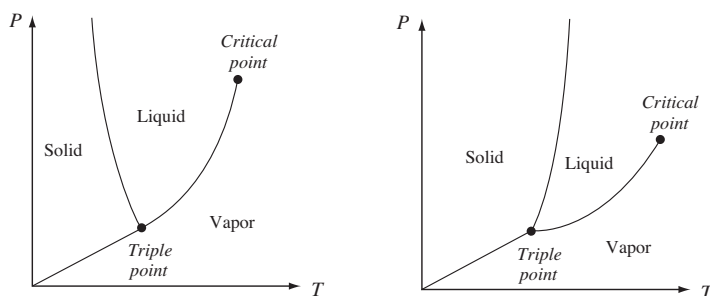


Figure 15.7: Phase diagrams for water (left) and other substances (right) show the pressure-temperature relations of the phase transitions solid-liquid, liquid-vapor, and solid-vapor. At the triple point, which has unique values of pressure and temperature, the three phases coexist. At temperatures (and pressures) above the critical point, liquid and vapor are indistinguishable.

For the third phase transition, sublimation, an analogous pressure-temperature relation exists. The three lines meet in a single point, the so-called triple point, where all three phases coexist. Drawing the three $P(T)$ functions leads to the phase diagrams shown in the graphs above.

15.1.2 Phase Transformations and Chemical Equilibrium

Phase changes can be understood in terms of chemical reactions (Chapter 6). If the chemical potential of a phase is higher at given pressure and temperature than that of another phase, the former will change into the latter. The conditions necessary for the changes to occur can therefore be found by considering chemical equilibrium between the phases. This section will show how easily the chemical potential may be used to understand phenomena related to phase transitions.

Melting and vaporization as chemical reactions. Phase changes can be viewed as a particular kind of chemical transformation, subject to the same laws we have studied in Chapter 6, where we were able to calculate what happens as a consequence of a chemical reaction on the basis of the chemical potentials of the substances. Here, the substances are solid (*s*), liquid (*l*), and gaseous water (*g*). If you look at Table 6.2, you see that at standard conditions, liquid water has the lowest chemical potential. This means that we should expect both ice and vapor to change into liquid water at a temperature of 25°C and a pressure of 1 atm.

The values of the temperature coefficients of the chemical potential found in Table 6.2 allow us to compute approximate values for the temperatures of the melting point and the point of vaporization, if the pressure remains constant. Points of phase transitions are obviously those where two phases coexist. If ice becomes liquid at a temperature of 25°C, because under this condition its chemical potential is larger than that of the liquid, we simply ask at which value of the temperature the tendency of water to change into ice has become equally large as the drive of ice to melt. In other words, we want to know the temperature for which the two chemical potentials have become equal:

$$\mu_{ice}(T_f, P_0) = \mu_{liquid}(T_f, P_0) \quad (15.6)$$

Since the potentials change with temperature according to Equ.(6.24), the condition expressed in this equation becomes

$$\mu_{ice}^0 + \alpha_{\mu,ice}(T - T_0) = \mu_{liquid}^0 + \alpha_{\mu,liquid}(T - T_0) \quad (15.7)$$

Solving this simple equation, we obtain 274.7 K for the melting point of water. Considering that this is just a linear approximation, the result is quite acceptable.

Pressure dependence of the melting point. The problem of the change with pressure of the melting point and the temperature of vaporization is even more interesting, since it involves both changes in pressure and in temperature. Again, the chemical potentials of liquid and solid (or gaseous) water have to be equal at the actual melting point (or point of vaporization), and again the potentials change with temperature, and this time also with pressure. Therefore, the following condition must be satisfied:

$$\begin{aligned} \mu_{ice}^0 + \alpha_{\mu,ice}(T - T_0) + \beta_{\mu,ice}(P - P_0) \\ = \mu_{liquid}^0 + \alpha_{\mu,liquid}(T - T_0) + \beta_{\mu,liquid}(P - P_0) \end{aligned} \quad (15.8)$$

For simplicity, assume the reference temperature to be the value of the melting point T_f at the reference pressure, in which case the standard potentials of ice and water are equal. With this in mind, we arrive at a relation between the change of pressure and temperature:

$$\frac{\Delta P}{\Delta T} = - \frac{\alpha_{\mu,liquid} - \alpha_{\mu,ice}}{\beta_{\mu,liquid} - \beta_{\mu,ice}} \quad (15.9)$$

Using the values for water from Table 6.2, we obtain an interesting result, which is that the melting point of ice decreases with increasing pressure (with the corresponding values at 0°C we get the result of $\Delta P/\Delta T = -135$ bar/K). This is so because the pressure coefficient of ice is larger than that of water, a condition which holds only for water, and maybe one or two other substances. Generally, the temperature of the melting point increases with increasing pressure. The same is true for the temperature of vaporization, which increases if more pressure is applied. This also holds for water: water boils at higher temperature if the pressure is increased (see the discussion about vaporization at different pressures presented below).

In Chapter 8, and again in Chapter 10 (Equations (10.51) and (10.52)), we saw that, at least for the bodies we have studied, the temperature coefficient of the chemical potential is the negative molar entropy of the substance, and the pressure coefficient is the molar volume. Applying this and writing l and s for liquid and solid, respectively, Equ.(15.9) becomes

$$\frac{\Delta P}{\Delta T} = \frac{\bar{s}_l - \bar{s}_s}{\bar{v}_l - \bar{v}_s} \quad (15.10)$$

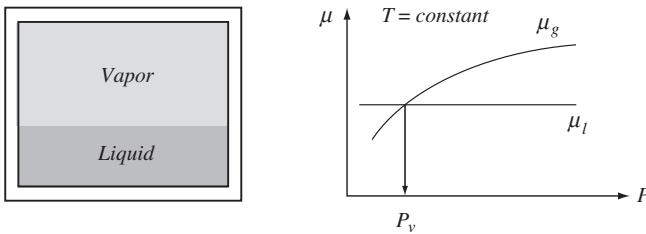
This result is of much more general importance than could be guessed from the derivation. It is called *Clapeyron's law*, and it shows that the change of pressure accompanying a change of temperature of phase transformation depends upon the entropy necessary for the phase change and the change of volume of the fluid (remember the formal derivation in Section 10.2.6). Another derivation of this result based on a cyclic process will be presented below. Note that you can apply Equ.(15.10) to vaporization

as well. Since the change of volume is much larger in vaporization, the change of pressure with a change of boiling point should be much less dramatic than what we have observed for melting ice.

15.1.3 Vapor Pressure

What is it that makes the states of saturated liquid or vapor special? What is the relation between the pressure of the fluid and the temperature at which it changes its phase? To answer these questions, consider some liquid put into an otherwise empty container. It is easy to see what happens if you place a drop of the liquid at the top of the mercury column in a pressure gauge (Fig. 15.8). Even though the weight of the drop is so small as not to add to the pressure of the column of mercury, the top of the mercury column is observed to go down; obviously, there is some fluid in the previously empty space at the top of the gauge which has a noticeable pressure. We interpret this observation by assuming that a part of the drop has vaporized, and the pressure of the vapor is responsible for the change of height of the mercury column. Naturally, the pressure of the remaining liquid at the top of the gauge is the same as that of the vapor, and this pressure is called the *vapor pressure* of the fluid. It is further observed that the vapor pressure depends only upon the temperature of the fluids involved, as long as there always is at least a little bit of liquid left. How can we understand this relation between the temperature of the fluids and the vapor pressure?

For a given temperature, after the physical variables have assumed constant values, the situation of the fluid and its vapor is that of an insulated system inside a container (Fig. 15.9). Since volume and energy are kept constant, the only possible changes in-



side the container are the transformation of vapor into liquid (or vice versa), and the production of entropy. According to Equ.(6.34), the entropy production rate equals

$$\Pi_S = \frac{1}{T} |\mu_g - \mu_l| |\dot{n}| \quad (15.11)$$

Assume for the moment that the chemical potential of the vapor is larger than that of the liquid. In this case, we expect some of the substance to go from the vapor into the liquid phase. Since this process will stop when equilibrium conditions have been reached, we have to conclude that the chemical potentials of the vapor and of the liquid phase have to be equal in equilibrium; it is equally likely for liquid to change into vapor as it is for vapor to condense:

$$\mu_g(P, T) = \mu_l(P, T) \quad (15.12)$$

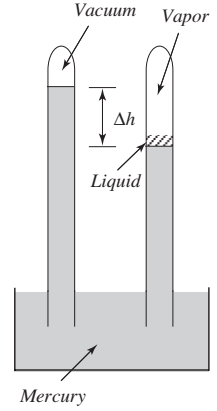


Figure 15.8: Detecting the pressure of the vapor which forms from the liquid at the top of a mercury gauge.

Figure 15.9: The chemical potential of the vapor inside the container changes much more strongly with pressure than the chemical potential of the liquid. Therefore, it is easy to conceive of conditions for which μ_g is either smaller or larger than μ_l . In the latter case, some of the vapor will condense. When the chemical potentials are equal, the phases are in equilibrium.

We can estimate the value of the vapor pressure of water at a temperature of 25°C from the values found in Table 6.2. With the temperature given, the values of the chemical potential depend only upon pressure. Since, in Table 6.2, they are given for the standard pressure of 1 atm, we have to change the potentials to the condition of the as yet unknown vapor pressure. If we treat water vapor as an ideal gas, and water as an incompressible fluid, we have

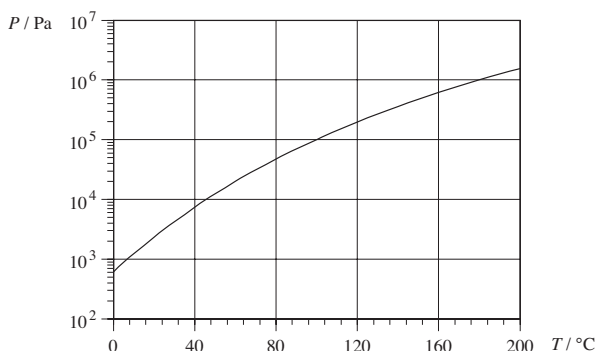
$$\mu_g^0 + RT \ln\left(\frac{P_v}{P_0}\right) = \mu_l^0 + (P_v - P_0)\bar{v}_{l0} \quad (15.13)$$

as the condition of chemical equilibrium between liquid water and its vapor at 25°C. If you plug in some values, you will notice that the pressure term for the liquid is very small compared to the other terms, which means that the actual pressure of the liquid does not greatly influence the result. (For example, giving the liquid a larger pressure than the value P in the diagram of Fig. 15.9 will shift the horizontal line upward by a very small amount.) The important parameter is the vapor pressure. Solving the condition for the value of P_v yields

$$\ln\left(\frac{P_v}{P_0}\right) = -\frac{1}{RT}(\mu_g^0 - \mu_l^0) \quad (15.14)$$

(see Fig. 15.10). With the values taken from Table 6.2, the vapor pressure of water at 298 K is estimated to be 3150 Pa. This is close to the measured value of 3169 Pa (see Table 15.1).

Figure 15.10: With increasing temperature, the vapor pressure of water rises rapidly. The values must be obtained from measurements, since the fluids do not obey simple constitutive relations. Note that, in order to obtain the vapor pressure at a certain temperature from a theoretical correlation such as Equ.(15.14), the chemical potentials have to be also adjusted for the temperature.



Interpreting the condition of equilibrium in Equ.(15.12), we conclude that a particular relation between temperature and pressure exists as long as there is equilibrium between the phases. The pressure of the vapor cannot be changed independently of temperature as in the case of a single phase gas with constant amount of substance. The main difference is that in this case the gas is in equilibrium with its condensate. When the temperature is increased, more vapor is added to the vapor phase; when the temperature is decreased, some of the vapor can change into the liquid phase. This free exchange of amount of substance is responsible for the fact that the vapor pressure of a substance is a unique function of temperature. The answer to the question posed at the beginning of the section can now be given: the points of the bell-shaped curve in

Fig. 15.5 are those for which the chemical potentials are the same at a given temperature. They correspond to the conditions of chemical equilibrium between liquid and vapor.

Table 15.1: Properties of saturated water (liquid–vapor)^a

T °C	P_v bar	$\mu_l = \mu_g$ kJ/kg	s_l kJ/K · kg	s_g kJ/K · kg	v_l^*1000 m ³ /kg	v_g m ³ /kg	e_l kJ/kg	e_g kJ/kg
0.01	0.00612	0.000	0.0000	9.1541	1.0002	205.987	0.00	2374.5
5	0.00873	−0.003	0.0763	9.0236	1.0001	147.0239	21.02	2381.4
10	0.01228	−0.014	0.1510	8.8986	1.0003	106.3229	41.99	2388.3
15	0.01706	−0.031	0.2242	8.7792	1.0009	77.8971	62.92	2395.2
20	0.02339	−0.054	0.2962	8.6651	1.0018	57.7777	83.83	2402.0
25	0.03169	−0.084	0.3670	8.5558	1.0030	43.3566	104.75	2408.9
30	0.04246	−0.120	0.4365	8.4513	1.0044	32.8955	125.67	2415.7
35	0.05627	−0.162	0.5050	8.3511	1.0060	25.2204	146.58	2422.5
40	0.07381	−0.211	0.5723	8.2550	1.0079	19.5283	167.50	2429.2
45	0.09590	−0.265	0.6385	8.1629	1.0099	15.2634	188.41	2435.9
50	0.12344	−0.326	0.7037	8.0745	1.0122	12.0367	209.31	2442.6
60	0.19932	−0.464	0.8312	7.9080	1.0171	7.6743	251.13	2455.8
80	0.47373	−0.807	1.0753	7.6112	1.0290	3.4088	334.88	2481.6
100	1.01322	−1.235	1.3069	7.3545	1.0434	1.6736	418.96	2506.1
120	1.98483	−1.743	1.5278	7.1297	1.0603	0.8922	503.57	2529.1
140	3.61195	−2.329	1.7394	6.9302	1.0797	0.5090	588.85	2550.0
160	6.17663	−2.987	1.9429	6.7503	1.1019	0.3071	674.97	2568.3
180	10.01927	−3.714	2.1397	6.5853	1.1273	0.1940	762.12	2583.4
200	15.53650	−4.508	2.3308	6.4312	1.1564	0.1273	850.58	2594.7
220	23.17846	−5.364	2.5175	6.2847	1.1900	0.0862	940.75	2601.6
240	33.44673	−6.281	2.7013	6.1423	1.2292	0.0597	1033.12	2603.1
260	46.89449	−7.256	2.8838	6.0009	1.2758	0.0422	1128.4	2598.4
280	64.13154	−8.287	3.0669	5.8565	1.3324	0.0302	1227.53	2585.7
300	85.83784	−9.371	3.2534	5.7042	1.4037	0.0217	1332.00	2562.8
320	112.79318	−10.506	3.4476	5.5356	1.4984	0.0155	1444.35	2525.2
340	145.94085	−11.691	3.6587	5.3345	1.6373	0.0108	1569.93	2463.9
360	186.55306	−12.924	3.9153	5.0542	1.8936	0.0070	1725.64	2352.2
370	210.29877	−13.558	4.1094	4.8098	2.2068	0.0050	1843.33	2235.2
373	217.98862	−13.751	4.2259	4.6537	2.4852	0.0041	1912.45	2153.2

a. Values computed according to the Steam-NBS function implemented in the program EES (Klein et. al, 1991).

Estimate of the temperature dependence of vapor pressure. We can get a first impression of the dependence of the vapor pressure on temperature, if we use the formulas for the temperature dependence of the ideal gas and incompressible fluids from Section 8.4. In other words, we treat the vapor as an ideal gas, and the liquid as incom-

pressible. With Equ.(8.54), the chemical potentials of the two fluids are

$$\begin{aligned}\mu_g &= \mu_g^0 + RT \ln\left(\frac{P_v}{P_0}\right) + \bar{c}_{pg}(T - T_0) - T \bar{c}_{pg} \ln\left(\frac{T}{T_0}\right) - (T - T_0)\bar{s}_{0g} \\ \mu_l &= \mu_l^0 + (P_v - P_0)\bar{v}_{0l} + \bar{c}_{pl}(T - T_0) - T \bar{c}_{pl} \ln\left(\frac{T}{T_0}\right) - (T - T_0)\bar{s}_{0l}\end{aligned}\quad (15.15)$$

The pressure term in the chemical potential of the liquid and the terms with the temperature coefficients of enthalpy are relatively small compared to the entropy terms. Accepting this additional approximation, the condition of equilibrium leads to

$$\ln\left(\frac{P_v}{P_0}\right) = -\frac{1}{RT} \left\{ (\mu_g^0 - \mu_l^0) - (T - T_0)(\bar{s}_{0g} - \bar{s}_{0l}) \right\} \quad (15.16)$$

We can use this result to compute the temperature for which the vapor pressure is the standard pressure of 1 atm. The values of Table 6.2 yield a temperature of 97°C, which is acceptably close to the actual value considering the approximations made.

15.1.4 The Clapeyron Equation

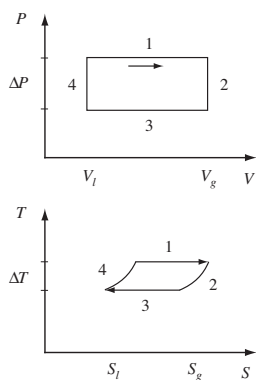


Figure 15.11: A pure simple fluid is allowed to go through a cycle including vaporization and condensation. The energy released in the fall of entropy is equal to the energy exchanged in the mechanical process. The curves are to be found in the bell-shaped area, where a mixture of liquid and vapor exists.

Considering that the vapor pressure is only a function of temperature, its values can be found. All we need to know are a starting value and the change of vapor pressure with temperature. As you will see shortly, the laws of thermodynamics provide for a relation between the derivative of the vapor pressure with respect to temperature and changes of properties of the fluid. The initial value is delivered by a single observation such as the one which tells us that at a temperature of 100°C the vapor pressure of water must be 1 atm.

In Section 10.2.6, a formal derivation of the following result was given. Here, we will consider a cyclic process of a substance which undergoes evaporation and condensation. Take a four step cycle which starts with the evaporation of a fluid at constant temperature and pressure (Fig. 15.11). The change of volume is from V_l to V_g , while the entropy changes from S_l to S_g (both changes are positive). Next, let the gas be cooled just a little bit at constant volume so that the temperature decreases by a very small amount ΔT . At this slightly lower temperature, allow the vapor to condense; this process will again take place at constant pressure. The volume returns to V_l , and very nearly the same amount of entropy is emitted as was absorbed during vaporization. This will be the case if the second step is made so small that it does not add considerably to the overall balances. Finally, the liquid is brought back to the initial state by a slight heating at constant volume.

The cycle described is that of a heat engine. We can evaluate the energy released in the fall of entropy, and the energy used for the mechanical process, and equate them (remember that steps 2 and 4 of the cycle do not contribute much to the balances):

$$(\bar{s}_g - \bar{s}_l)\Delta T = (\bar{v}_g - \bar{v}_l)\Delta P \quad (15.17)$$

This is the relation between changes of temperature and changes of vapor pressure we have been looking for; it can be brought into the form known as *Clapeyron's equation*:

$$\frac{dP}{dT} = \frac{\bar{s}_g - \bar{s}_l}{\bar{v}_g - \bar{v}_l} \quad (15.18)$$

If you wish, you can express the change of the entropy from the liquid to the vapor state using the enthalpy of the fluid, Equ.(15.5).

QUESTIONS

1. When water is evaporated, how much of the added entropy and energy will be in the steam?
2. What can be said about the chemical potentials of liquid and vapor (or solid and liquid) along the corresponding pressure-temperature function separating the phases in the PT phase diagram of Fig. 15.7?
3. Consider the TS diagram of the phase transition from liquid to vapor in Fig. 15.5. At which points or along which lines are the chemical potentials of liquid and vapor equal?
4. If the vapor pressure curve for water is to be calculated on the basis of the models of incompressible fluid and ideal gas, which relations must be used?

EXAMPLE 15.1. Change of melting point of water with a change of pressure.

Determine the change of pressure accompanying a change of the melting point of ice. (a) Calculate the temperature and the pressure coefficients of the chemical potential of water and ice for 0°C , and then use Clapeyron's equation. The temperature coefficients of enthalpy of water and of ice are $4200 \text{ J/(K} \cdot \text{kg)}$ and $2100 \text{ J/(K} \cdot \text{kg)}$, respectively. (b) Use the fact that the energy needed to melt ice is 334 kJ/kg . (See also Example 6.5.)

SOLUTION: (a) Modeling water and ice as bodies with constant temperature coefficients of enthalpy, we can calculate their change of entropy from standard temperature to 0°C :

$$\bar{s}(T_f) = \bar{s}_0 + \bar{c}_p \ln\left(\frac{T_f}{T_0}\right)$$

Considering that the molar entropy is the negative temperature coefficient of the chemical potential given in Table 6.2, we obtain for it:

$$\bar{s}(0^\circ\text{C}) = 44.8 + 0.018 \cdot 2100 \cdot \ln\left(\frac{273}{298}\right) = 41.5 \frac{\text{J}}{\text{K} \cdot \text{mole}}$$

For liquid water, the figure is $63.3 \text{ J/(K} \cdot \text{mole)}$. Note that the pressure coefficients of the chemical potential, i.e., the molar volumes, of ice and of water will not change much from their values in Table 6.2. Now, with Equ.(15.9), the result is

$$\frac{\Delta P}{\Delta T} = -\frac{\alpha_{\mu, \text{liquid}} - \alpha_{\mu, \text{ice}}}{\beta_{\mu, \text{liquid}} - \beta_{\mu, \text{ice}}} = -\frac{-63.3 - (-41.5)}{(18.1 - 19.7) \cdot 10^{-6}} \frac{\text{Pa}}{\text{K}} = -1.36 \cdot 10^7 \frac{\text{Pa}}{\text{K}}$$

(b) Starting with Clapeyron's equation in the form of Equ.(15.10), we see that the right-hand side can be expressed in terms of the energy supplied to ice as it melts. The entropy and the energy necessary for melting are related by Equ.(15.5), which means that Clapeyron's equation can be written as follows:

$$\frac{\Delta P}{\Delta T} = \frac{\bar{s}_l - \bar{s}_s}{\bar{v}_l - \bar{v}_s} = \frac{1}{T_f} \frac{\bar{h}_l - \bar{h}_s}{\bar{v}_l - \bar{v}_s} = \frac{1}{T_f} \frac{\Delta \bar{h}_{\text{fusion}}}{\bar{v}_l - \bar{v}_s}$$

With the value of the latent enthalpy of fusion, we obtain -138 bar/K for $\Delta P/\Delta T$.

EXAMPLE 15.2. Changes of vapor pressure and enthalpy of vaporization.

(a) Express the approximate result for vapor pressure as a function of temperature in terms of the change of the enthalpy of vaporization. Use the temperature of vaporization at 1 atm as a reference. (b) Determine the vapor pressure and the standard chemical potential of mercury vapor at 25°C .

SOLUTION: (a) First, with a pressure of 1 atm and its corresponding temperature of vaporization as the reference point, the standard chemical potentials of vapor and liquid are equal. Using the relation between the entropy and the enthalpy of vaporization leads to

$$\ln\left(\frac{P_v}{P_o}\right) = \frac{1}{R}\left(1 - \frac{T_{bp}}{T}\right)(\bar{s}_{bp,g} - \bar{s}_{bp,l}) = \frac{1}{R}\left(\frac{1}{T_{bp}} - \frac{1}{T}\right)\Delta\bar{h}_{v, bp}$$

where *bp* stands for *boiling point*. This means that a measurement of the enthalpy of vaporization yields fundamental information about a fluid (as an ideal gas).

(b) We can apply the result just obtained with $T_{bp} = 630 \text{ K}$, and 57 kJ/mole for the molar enthalpy of vaporization. This leads to

$$\ln\left(\frac{P_v}{P_o}\right) = \frac{1}{8.31}\left(\frac{1}{630} - \frac{1}{298}\right)57000 = -12.1$$

or $P_v = 0.54 \text{ Pa}$. This value, in turn, can be used to calculate the chemical potential of gaseous mercury at 25°C and 1 atm. We use the same derivation which led to Equ.(15.14):

$$\ln\left(\frac{P_v}{P_o}\right) = -\frac{1}{8.31 \cdot 298}(\mu_g^0 - 0)$$

Remember that the standard value of the chemical potential of liquid mercury is set equal to zero. This gives a value of $+30.0 \text{ kJ}$ (compared to the more accurate figure of 31.84 kJ).

EXAMPLE 15.3. The Clausius-Clapeyron equation for the ideal gas.

Derive the expression of the Clapeyron equation as it holds for the ideal gas and show that this is equivalent to the approximation of the pressure-temperature relation for vapor pressure derived in Equ.(15.16) or above in Example 15.2. Assume the enthalpy of vaporization to be constant.

SOLUTION: Written using the enthalpy of vaporization, Clapeyron's equation becomes

$$\frac{dP}{dT} = \frac{\bar{s}_g - \bar{s}_l}{\bar{v}_g - \bar{v}_l} = \frac{1}{T} \frac{\bar{h}_g - \bar{h}_l}{\bar{v}_g - \bar{v}_l} = \frac{1}{T} \frac{\Delta\bar{h}_v}{\bar{v}_g - \bar{v}_l}$$

For the ideal gas, we use the equation of state, and we neglect the volume of the liquid phase compared to its value in the vapor phase. Therefore, the equation becomes

$$\frac{dP}{dT} = \frac{1}{T} \frac{\Delta\bar{h}_v}{\bar{v}_g} = \frac{1}{T} \frac{\Delta\bar{h}_v}{RT/P} = \frac{P}{RT^2} \Delta\bar{h}_v$$

Integration of this equation yields

$$\ln\left(\frac{P}{P_0}\right) = \frac{1}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \Delta \bar{h}_v$$

which is equivalent to what was derived before. Clapeyron's equation specialized to the ideal gas is called the Clausius-Clapeyron equation.

15.2 MIXTURES OF TWO-PHASE FLUIDS: MOIST AIR

In this section, we will discuss one more application of the ideas of chemical transformation, namely the thermodynamics of mixtures of two ideal gases when one can undergo phase changes. Moist air furnishes such an example—dry air and water vapor. While the air itself is a mixture, it can be treated as a single component, since in the range of temperature and pressure found in our atmosphere, its constituents all behave identically as ideal gases; in other words, we do not notice that dry air itself is composed of different parts. The case of the second component, however, is quite different. With liquid (or solid) water present, water vapor in the air can condense (or directly turn into frost or ice); or water can evaporate (and ice can sublime). Thus, the conditions in the atmosphere are such that water can undergo phase transitions. We are all familiar with water condensing on window panes on a cold day, droplets forming on a pipe carrying cold water, dew accumulating on the grass in the morning, or frost forming on the ground.

These and their reverse processes can again be understood as chemical phenomena. When vapor condenses out of moist air, this simply means that, under the given circumstances, the chemical potential of the water vapor is larger than that of the liquid phase. On the other hand, when water evaporates from the surface of a pond, the tendency of liquid to go into the vapor phase is stronger than the reverse drive.

We can use our knowledge of the concepts of vapor pressure and chemical equilibrium between phases to state these observations in more precise language. Consider evaporation of water into the air above a liquid surface (as in Fig. 15.12). Obviously, if water diffuses from the liquid into the air, chemical equilibrium has not been attained. There is less water vapor in the air than there could be under the condition of equilibrium, or, put differently, the gas above the water surface is said to have a humidity which is smaller than the humidity at saturation. When the air is saturated with water vapor, the chemical potential of the vapor phase and of the liquid phase are equal, and there are equal rates of water evaporating and vapor condensing.

To give you an impression of the amount of water vapor present in the air, consider standard conditions of temperature and pressure. You know that at 25°C, the vapor pressure of water is about 3000 Pa or 0.030 bar (see Table 15.1). As we have seen before, it hardly matters that the pressure of the liquid is 1 atm because of the presence of the air: the chemical potential of liquid water changes only slightly when its pressure changes. Therefore, the value of the vapor pressure calculated under the assumption that only water is present can be used perfectly well in the present case. We can now say that at saturation the amount of water in the air is 0.03 mole per 1 mole of air (equivalent to about 20 g of H₂O in 1 m³ of air). With such numbers, it is clear that the vapor component also behaves as an ideal gas. As far as the body of moist air is concerned, we can treat it as a mixture of two ideal gases and apply the rules found in Section 6.6.3.

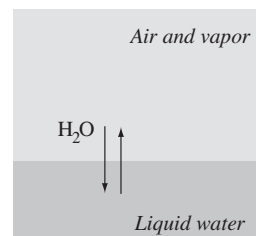


Figure 15.12: If a mixture of dry air and water vapor is present together with liquid water, the vapor component of the gas can undergo phase transitions. At chemical equilibrium, the air is said to be saturated with water vapor.

15.2.1 Description of the State of Moist Air

It is customary to define two interrelated quantities with whose help the state of moist air can be described. These are the *humidity ratio* (also called specific humidity or absolute humidity), and the *relative humidity*. First, it should be clear that the pressure of the mixture is P , while the partial pressures of dry air and of vapor are P_a and P_v , respectively, with

$$P = P_a + P_v \quad (15.19)$$

The humidity ratio ω is defined as the ratio of the mass of water vapor m_v and the mass of dry air m_a .¹

$$\omega \equiv m_v/m_a \quad (15.20)$$

Using the equation of state of the ideal gas this can be transformed into

$$\omega = \frac{M_{0v}P_v}{M_{0a}P_a} = 0.622 \frac{P_v}{P - P_v} \quad (15.21)$$

The numerical value 0.622 applies for dry air and water. The second quantity introduced, the relative humidity ϕ , is defined as the ratio of the amount of water vapor actually present and the amount present when the air is saturated with vapor:

$$\phi \equiv n_v/n_{v,sat} \quad (15.22)$$

The laws of ideal gases let us change this to

$$\phi = \frac{y_v}{y_{v,sat}} = \frac{P_v}{P_g} \quad (15.23)$$

where P_g is the saturation vapor pressure at the temperature under consideration (in the following, the index g will be used to indicate saturation). Note that the relative humidity and the humidity ratio are convenient definitions for expressing the case of moist air in terms of the laws of mixtures of ideal gases introduced in Section 6.6.3. As far as physics is concerned, nothing new has been formulated. What we can say, however, is that at a relative humidity smaller than 1, the chemical potential of the vapor μ_v is smaller than its value for the condition at saturation μ_g , the change stemming from the difference in actual vapor pressure from the saturation pressure. Therefore

$$\mu_v = \mu_g + RT \ln \phi \quad (15.24)$$

Since the temperature is the same for the actual condition and for the assumed condition of saturation, the enthalpy of the vapor is what it would be at saturation:

1. Sometimes, the specific humidity is defined as the ratio of mass of water vapor m_v to mass of (humid) air m :

$$\omega \equiv m_v/m$$

and therefore differs slightly from the humidity ratio.

$$h_v = h_g \quad (15.25)$$

This holds for an ideal gas (see Fig. 15.29 for actual values). Therefore, the entropy of the vapor (s_v), deviates from its value at saturation (s_g):

$$\bar{s}_v = \bar{s}_g - R \ln \phi \quad (15.26)$$

15.2.2 The Dew Point

Assume a state of moist air with a relative humidity less than the saturation value of 1. This means that the chemical potential of the vapor at the given temperature is smaller than the potential of the liquid phase (Fig. 15.13). Now, what happens if the temperature of the mixture and the liquid water decreases? The chemical potentials of the vapor and the liquid phase increase, but not at the same rate. From Table 6.2, we see that the magnitude of the slope for the gaseous phase is greater, which means that the potentials become equal at a particular value of the temperature. At this point, water vapor in the air will begin to condense. For obvious reasons, this temperature is called the *dew point*. Using a table of saturation vapor pressure, dew points can be easily computed (Example 15.4). Here, we will give a formal derivation assuming the validity of the ideal gas model.

We have to find the temperature for which the chemical potentials of the vapor in the air and of the liquid water phase are equal, given a starting condition at temperature T_0 and pressure P_0 . The chemical potential of the liquid changes from the standard value only because of the change of temperature:

$$\mu_l(T_d) = \mu_l^0 - (T_d - T_0)\bar{s}_{0l} \quad (15.27)$$

The potential of the vapor, on the other hand, is different from the standard value for two reasons: the pressure P_v at temperature T_0 is different from P_0 ; and the temperature is now at the dew point:

$$\mu_v(T_d) = \mu_g^0 + RT_d \ln\left(\frac{P_v}{P_0}\right) - (T_d - T_0)\bar{s}_{0g} \quad (15.28)$$

Now, the actual vapor pressure P_v can be expressed in terms of the saturation value if we introduce the relative humidity:

$$\begin{aligned} \mu_v(T_d) &= \mu_g^0 + RT_d \ln\left(\frac{\phi P_{g0}}{P_0}\right) - (T_d - T_0)\bar{s}_{0g} \\ &= \mu_g^0 + RT_d \ln\left(\frac{P_{g0}}{P_0}\right) + RT_d \ln \phi - (T_d - T_0)\bar{s}_{0g} \end{aligned} \quad (15.29)$$

Equating the chemical potentials, i.e., Equations (15.27) and (15.29), furnishes a non-linear condition for the unknown temperature of the dew point. We need only the saturation pressure P_{g0} at the original temperature T_0 , which can be calculated from the approximation given in Equ.(15.16) or found in tables. The formulas are rather accurate, and compare well with the measured values found in steam tables. Remember

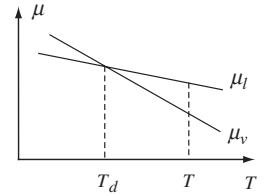


Figure 15.13: At a value of the relative humidity which is less than 1, the chemical potential of the vapor is smaller than that of liquid water. Decreasing the temperature leads to a condition for which the potentials are equal: condensation of water vapor sets in.

that, apart from the assumption of validity of the ideal gas model, we have neglected some terms in the temperature dependence of the chemical potentials.

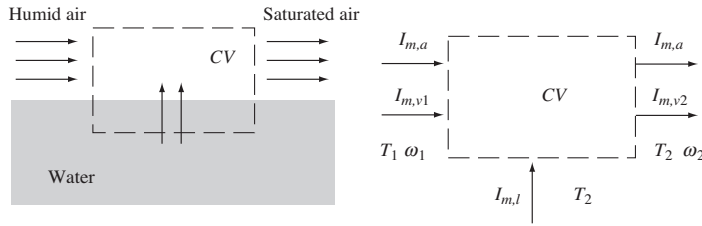
15.2.3 Adiabatic Saturation and Wet Bulb Temperature

Below, an equation will be used that relates the humidity ratio of moist air to the wet bulb temperature. The process taking place around a wet bulb thermometer is similar to the model of adiabatic saturation that will be discussed now.

Adiabatic saturation. Take a stream of moist air passing over the surface of some water as in Fig. 15.14. The air picks up extra moisture until it is saturated. Since no conductive transfer of entropy is involved, the process is called *adiabatic saturation*. Consider a control volume encompassing a section of the air stream and a small part of the water which delivers the moisture. In a steady state, the amount of water vapor flowing out with the saturated air will be the sum of the mass entering with the somewhat dryer air, and the mass of the water evaporating from the surface (this latter mass is replenished through the control surface):

$$|I_{m,a}| + |I_{m,v1}| + |I_{m,l}| = |I_{m,a}| + |I_{m,v2}| \quad (15.30)$$

Figure 15.14: A stream of moist air passes over a water surface and picks up additional water until it is saturated. The air cools to T_2 , and in the steady state, the water will have the same temperature (if the body of water is not too large).



Here, a , l , and v denote dry air, liquid water, and water vapor, respectively. For the balance of energy, we will assume the velocity terms to be negligible. Also, the moist air will be considered to be a simple mixture of dry air and water vapor at total pressure P . At the inlet, the temperature is T_1 , and the humidity ratio is ω_1 , while at the outlet we have T_2 and ω_2 (in the saturation process, the incoming air is assumed to cool to the temperature of the water which is at T_2). Now, the energy currents can be written in terms of the enthalpy of the fluids (see Equ.(8.40)):

$$h_a(T_1)|I_{m,a}| + h_v(T_1)|I_{m,v1}| + h_l(T_2)|I_{m,l}| = h_a(T_2)|I_{m,a}| + h_g(T_2)|I_{m,v2}| \quad (15.31)$$

As before, the index g is used for the saturated vapor state. Using the balance of mass we can express the current of water from the reservoir. Dividing by the current of mass of dry air introduces the humidity ratio. If we also replace the enthalpy of the unsaturated vapor at T_1 by the corresponding value for the saturated state at T_2 (remember Equ.(15.25)), we get:

$$h_a(T_1) + \omega_1 h_g(T_1) + (\omega_2 - \omega_1) h_l(T_2) = h_a(T_2) + \omega_2 h_g(T_2) \quad (15.32)$$

Wet bulb temperature. The condition of an ideal gas of constant amount of substance is fixed by two values such as the pressure and the temperature. A third value is obvi-

ously needed if a mixture such as moist air is described for which the amount of vapor can change. A suitable third value might be the humidity ratio. However, humidity is not so readily measured, which is why it would be simpler to specify an additional temperature. Here, we will show how the temperature measured by a thermometer whose bulb is surrounded by a wet wick can be used to find the humidity of the air.

The temperature measured by a simple thermometer is called the dry bulb temperature of the moist air. If you surround the bulb of the thermometer with a wick saturated with water, it will show a lower temperature for the same conditions of the air, the value being called the wet bulb temperature (Fig. 15.15). The reason for the lower temperature is this: As the air, which is assumed to be not saturated, passes over the bulb with the wick, water will evaporate, increasing the humidity of the air. Indeed, we will assume the air to become saturated by the process—analogous to the process of adiabatic saturation discussed above, meaning that the saturated air has the same temperature as the water. The entropy necessary to vaporize the water in the wick comes from the water and from the air itself, which means that the temperature of the stream of air leaving the wick is lower than the normal air temperature. This new temperature is the temperature taken by the water in the wick; therefore, the wet bulb thermometer shows the lower temperature of the saturated air.

If the wet bulb thermometer is ventilated properly, the process taking place here is a close approximation to *adiabatic saturation*. It is specified by the temperatures and humidities of the original moist air and of the saturated air. The value of the humidity ratio can then be calculated from Equ.(15.32):

$$\omega = \frac{h_a(T_{wb}) - h_a(T) + \omega' [h_g(T_{wb}) - h_l(T_{wb})]}{h_g(T) - h_l(T_{wb})} \quad (15.33)$$

where ω' is computed according to Equ.(15.21) for the saturated air at the wet bulb temperature, i.e.,

$$\omega' = 0.622 \frac{P_g(T_{wb})}{P - P_g(T_{wb})} \quad (15.34)$$

The condition of adiabatic saturation may be satisfied by the wet bulb thermometer only to a limited extent. The real wet bulb phenomenon is influenced by the rate of evaporation and the rate of diffusion through the wick. Still, the agreement is acceptable, and the wet bulb temperature is commonly used as the representation of the adiabatic saturation temperature.

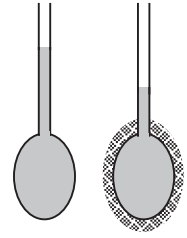


Figure 15.15: Dry and wet bulb thermometers for measuring the humidity of air. A wick saturated with water surrounds the second thermometer. If the air is not saturated, this thermometer will show a lower temperature than the dry bulb instrument.

QUESTIONS

5. In general, is the molar entropy of water vapor in the air smaller than, equal to, or larger than at saturation? Why is this so?
6. Why is moist air less dense than dry air (at the same temperature and pressure)? What does this mean for moist air coming off vegetation, the ground, or lakes?
7. Why can we assume that the enthalpy of water vapor in moist air is generally equal to the enthalpy of the vapor if the air is saturated with moisture?
8. In practice, what is the condition for the stream of air exiting the adiabatic saturator in Fig. 15.14 to be saturated and have the same temperature as the water (T_2)?

EXAMPLE 15.4. Calculating a dew point using tabular data.

(a) At a temperature of 30°C and standard pressure, the relative humidity of air is measured at 75%. Determine the temperature at which water vapor would begin to condense. Use the data given in Table 15.1. (b) The temperature of the air drops to 20°C. What fraction of the vapor present in the air will condense?

SOLUTION: (a) At 30°C, the saturation vapor pressure is 4246 Pa. With a relative humidity of 75%, the actual vapor pressure (the partial pressure of the water vapor in the air) is

$$P_v = \phi P_g = 0.75 \cdot 4246 \text{ Pa} = 3185 \text{ Pa}$$

The value of 3185 Pa almost precisely corresponds to the saturation vapor pressure at 25°C. This means that at 25°C, the air would be saturated with the amount of water vapor it actually contains, and the vapor would begin to condense.

(b) At 25°C and with a vapor pressure of 3185 Pa, the air could just retain the initial amount of water present at a relative humidity of 100%. At 20°C, however, the vapor pressure is only 2340 Pa. If we allow for 100% relative humidity at that state, the air could contain only the fraction $2340/3190 = 0.73$ of the initial amount of water. An initial amount of

$$n_{vo}/V = \frac{P}{RT} = \frac{3184}{8.314 \cdot 298} \frac{\text{mole}}{\text{m}^3} = 1.29 \frac{\text{mole}}{\text{m}^3}$$

will be reduced to 0.94 mole/m^3 . For every cubic meter of air, 6.3 g of water will condense.

EXAMPLE 15.5. The height above ground of cloud formation

Make the following model of the vertical circulation of air. Moist air (not saturated) rises adiabatically due to convective instability. With a relative humidity of 0.50, and standard pressure and temperature at the ground, calculate the level above ground at which condensation of the water vapor should set in. Explain why this happens for a temperature which is lower than the dew point calculated for the ground.

SOLUTION: The quantities which are constant for the process are the entropy and the humidity ratio. (Before the onset of condensation, the amount of water vapor in the air remains constant.) One therefore should calculate these two quantities for the conditions at the ground. In functional form, this might look like

$$so = \text{Entropy}(\text{AirH}_2\text{O}, T=298, P=100, R=0.5)$$

$$w = \text{HumRat}(\text{AirH}_2\text{O}, T=298, P=100, R=0.5)$$

Tables (or computer programs) yield values of $5.788 \text{ kJ/(K} \cdot \text{kg)}$ and 0.00992 , respectively. After this preparation, values of the temperature, and the specific volume can be taken from tables as a function of decreasing pressure. Again, using functions implemented in EES (Klein et al., 1991), we have

$$so = \text{Entropy}(\text{AirH}_2\text{O}, T=T, P=P, w=w)$$

$$v = \text{Volume}(\text{AirH}_2\text{O}, T=T, P=P, w=w)$$

Then, using the law of hydrostatic equilibrium, the volume can be integrated over the pressure to yield the height as a function of pressure:

$$dh/dP = -1/g\rho = -v/g$$

Finally, the chemical potential of liquid water and of water vapor have to be expressed:

$$\mu_l = \text{Mo}^*(\text{Enthalpy}(\text{Water}, T=T, X=0) - T^* \text{Entropy}(\text{Water}, T=T, X=0))$$

$$\mu_{v} = Mo*(Enthalpy(Water,T=T,P=P_v)-T*Entropy(Water, T=TP=P_v))$$

$$w = 0.622*P_v/(P-P_v)$$

Results are given in Table 15.2 and in the accompanying graph (Fig. Ex.5.1). The graph shows that, up to a certain height (about 1400 m, temperature of 284.5 K), the chemical potential of the vapor is smaller than that of liquid water (the chemical potential of liquid water increases because of the effect of decreasing temperature). At this point, the relative humidity becomes 1. We therefore expect cloud formation to begin at about this level above ground.

Table 15.2: Properties of moist air at constant entropy and humidity ratio

P / kPa	T / K	v / m ³ /kg	h / m	μ_l / kJ	μ_v / kJ
100	298.0	0.869	0	-0.0838	-1.7880
98	296.3	0.882	178	-0.0729	-1.5647
96	294.6	0.895	360	-0.0625	-1.3383
94	292.8	0.909	543	-0.0527	-1.1085
92	291.0	0.923	730	-0.0436	-0.8752
90	289.2	0.937	920	-0.0350	-0.6382
88	287.4	0.952	1110	-0.0271	-0.3976
86	285.5	0.968	1310	-0.0200	-0.1530
84	283.6	0.985	1510	-0.0135	-0.0135

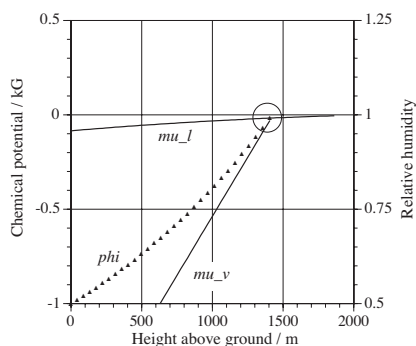


Figure Ex.5.1

The dew point calculated for the values at the ground, on the other hand, is 286.9 K. A plot of the chemical potential of liquid water and water vapor as a function of temperature can demonstrate the influence of a change of pressure upon the dew point. Lowering the pressure leaves the potential of the liquid more or less unchanged, while that of the vapor decreases. This shifts the line representing the chemical potential of the vapor downward, leading to an intersection with the line for the liquid at a lower temperature.

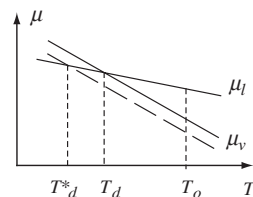


Figure Ex.5.2

EXAMPLE 15.6. Calculating the wet bulb temperature of moist air.

Take the same conditions for moist air as in Example 15.4 (75% relative humidity at 30°C and 1 atm). How large is the corresponding wet bulb temperature?

SOLUTION: In addition to the definition of relative humidity in terms of the vapor pressure and the saturation vapor pressure, we will need to simultaneously solve Equ.(15.21), Equ.(15.33) and Equ.(15.34). For the stated problem, namely finding the wet bulb temperature, the equations are nonlinear. We will have to find the values of enthalpies and pressures for the quantities appearing in the equations, partly for the still unknown value T_{wb} . Below you will find the relations to be set up if the thermodynamic property data are given in the form of programmed functions. Compare the solution of these equations with a solution attempted using tabulated values.

```

Given data:  phi = 0.75
              T1 = 30
              P1 = 101.3

Properties:   ha_T = Enthalpy(Air,T=T1)
              ha_Twb = Enthalpy(Air,T=Twb)
              hg_T = Enthalpy(Steam,T=T1,X=1),
              hg_Twb = Enthalpy(Steam,T=Twb,X=1)
              hl_Twb = Enthalpy(Steam,T=Twb,X=0)
              Pg_Twb = Pressure(Steam,T=Twb,X=1)
              Pg_T = Pressure(Steam,T=T1,X=1)

Relations:   w = ((ha_Twb-ha_T)+w'*(hg_Twb-hl_Twb))/(hg_T-hl_Twb)
              w' = 0.622*Pg_Twb/(P1-Pg_Twb)
              w = 0.622*Pv_T/(P1-Pv_T)
              phi = Pv_T/Pg_T

Solution:     ha_T = 303.6 kJ/kg      ha_Twb = 299.9
              hg_T = 2555              hg_Twb = 2549
              hl_Twb = 110.2
              P1 = 101.3 kPa          Pg_T = 4.246
              Pg_Twb = 3.425          Pv_T = 3.184
              phi = 0.750
              T1 = 30.0°C             Twb = 26.3
              w = 0.0202              w' = 0.0218

```

The solution of the problem was performed completely within the program EES (Klein et al., 1991). The form of the property functions is pretty much self explanatory. *Air* stands for dry air, while *Steam* denotes water (liquid and vapor). The temperature and its wet bulb counterpart are denoted by T and Twb , respectively, while w is used for the humidity ratio. X is the quality (defined in Equ.(15.59); $X=0$ is for saturated liquid, while $X=1$ is for saturated vapor).

15.3 EVAPORATION

The term evaporation is most commonly used to describe vaporization of some water from a larger body of water and subsequent transfer of the vapor into the air surrounding the body of water. In this section, evaporation or condensation of water, and the mixing of water vapor with air will be considered from a dynamical perspective. Such processes are important in nature (think of the evaporation of water from lakes, from soil, or from leaves), in chemical engineering (where we let other substances evaporate as well), in power engineering (cooling towers), and in air conditioning.

15.3.1 Evaporation and Diffusion of Water Vapor in Air

Consider a body of water with unmoving air above it. If the air is not saturated, there is a difference of chemical potentials between the liquid water and the water vapor in the air leading to the transfer of more water vapor into the air. Water must evaporate, so the concentration of vapor will be higher in a layer adjacent to the body of water than further away from it. As a result, the vapor diffuses upward into the drier air (see Fig. 15.16).

This process continues until the air above the water is saturated. If it is continuously removed—which normally is the case in an open space—evaporation from the surface of the body of water continues as long as liquid water remains. Evaporation does not depend upon the water being warmer than the air. In fact, the process described works even when the water is cooler than the air. All that is needed is a higher concentration of water vapor near the surface of the water compared to points further away.

Evaporation of warm water: a simple model. Hot water is poured into a glass and placed on a scale. The water stands at a depth d from the top of the container (see Fig. 15.17, left). Mass, water and air temperature, and relative humidity are measured as functions time. The temperature decreases as a result of cooling (Fig. 15.17, right) which is mostly due to evaporation: the mass of the water decreases quite steeply at higher temperatures whereas the flow of vapor into the air decreases to a lower and almost constant value for water temperatures close to the temperature of the air (see Fig. 15.17, center).

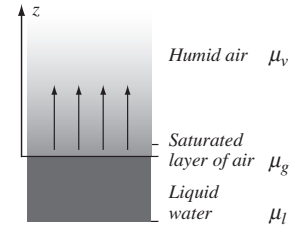
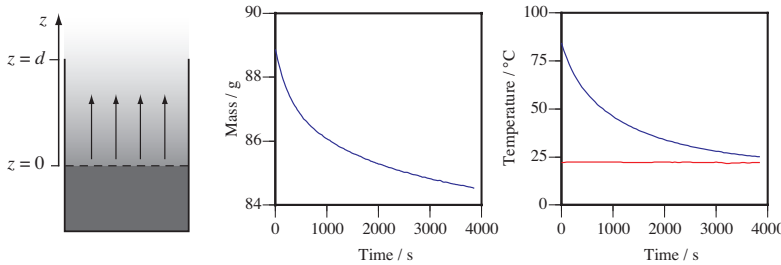


Figure 15.16: Evaporation from a body of water can be understood as the diffusion of water vapor from a saturated layer of air near at the surface of the water to points further away where the air is not saturated.

Figure 15.17: Evaporation of water in a glass open at the top (left). Mass (center) and water and air temperature (right) have been measured as functions of time. The relative humidity during the experiment was 0.20.

If evaporation is due to the diffusion of vapor from the surface of the liquid at $z = 0$ a distance d through the air, we can formulate a simple relation for the flow of amount of substance of water vapor (remember Section 6.7):

$$I_{n,v} = -Ah_v(\bar{c}_d - \bar{c}_0) \quad (15.35)$$

Here, \bar{c} stands for the concentration of vapor in the air at $z = d$ and $z = 0$, respectively. h_v is transfer coefficient for amount of substance, and A symbolizes the cross section of the water surface. If we treat the vapor as an ideal gas, its concentration is proportional to its partial pressure. Therefore, Equ.(15.35) transforms into

$$I_{n,v} = -\frac{Ah_v}{RT_a}(\phi P_g(T_a) - P_g(T_w)) \quad (15.36)$$

P_g is the saturation vapor pressure and ϕ denotes the relative humidity. Here, I have

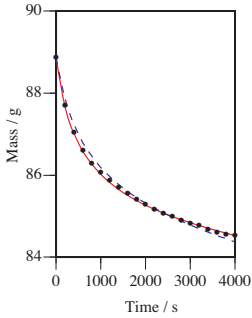


Figure 15.18: Evaporation of hot water from an open container as in Fig. 15.17. Dots are measured values of the mass of the remaining water. The dashed line is the result of the model presented in Equ.(15.36). The solid line results from a version of the model in Equ.(15.44).

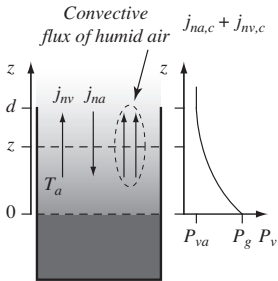


Figure 15.19: Evaporation of water in a container as in Fig. 15.17. There are several different currents of vapor and air (left). The diagram on the right shows the form of the vapor pressure in the column of air.

assumed that the vapor is always at the temperature of the air, T_a , even near the surface of the water which is at T_w . In the layer at the surface of the body of water, the air is saturated. The transfer coefficient h_v will depend upon the depth of the water in the container, and upon the diffusivity of water vapor in air.

If the measured temperatures (Fig. 15.17) are used to predict the flow of mass $I_{m,v} = M_{0v} I_{m,v}$ from the surface of the water, we get the dashed line shown in Fig. 15.18; at first sight, it compares relatively well with the measured mass (dots) but clearly shows different behavior. For this reason, let us extend the model to one which includes the spatial variation of conditions in the container of Fig. 15.17.

Diffusion of vapor in air. First, we have to understand the precise nature of the transports in the container of Fig. 15.17 in the column of moist air above the body of water. Let us assume that there is variability in the vertical direction only, and that the situation is in steady-state. There must certainly be a conductive (diffusive) flux of water vapor whose current density of amount of substance at a point z in the column of humid air will be abbreviated by j_{nv} (Fig. 15.19). In a mixture of gases such as dry air and water vapor, if one of the components diffuses in one direction, there must be an equal diffusive flux of the other component in the opposite direction. This is so because, in steady-state, one mole (or one molecule) of vapor must be replaced by one mole (or one molecule) of air. So we have a current density of dry air j_{na} at point z .

The downward flux of air has important consequences. If there were nothing to balance it, air would accumulate at the surface of the water. Since this is not the case, we need a convective (or bulk) flux of humid air going up where the flux of (dry) air must equal the diffusive downward flux of (dry) air. Since the air is humid, water vapor is transported convectively, so we have an additional flux of water vapor going upward (see Fig. 15.19).

The laws of balance of amounts of substance (of air and of water vapor) and coupling between the fluxes can be formulated quite simply. First, we should note that the fluxes are independent of position z since we have steady-state conditions. Second, the diffusive flux density of air is equal in magnitude to the diffusive flux density of water vapor:

$$j_{nv}(z) = -j_{na}(z) \quad (15.37)$$

Since air has to remain balanced in the column above the body of water, we have

$$j_{na,c}(z) = -j_{na}(z) \quad (15.38)$$

The subscript c stands for convective transports. Finally, there is the convective transport of vapor which is coupled to the convective flux of air. Since the amount of vapor in the air equals the molar fraction of the amount of humid air, we have

$$j_{nv,c}(z) = \bar{x}_v (j_{na,c}(z) + j_{nv,c}(z)) \quad (15.39)$$

(The current of humid air equals the sum of currents of air and vapor.) Now, the total current density of vapor is the sum of its diffusive and convective parts which leads to:

$$j_{nv,tot}(z) = \frac{1}{1 - \bar{x}_v} j_{nv}(z) \quad (15.40)$$

Now, constitutive relations have to be introduced. For one, the diffusive current density of vapor can be formulated as in Section 6.7.2:

$$j_{nv}(z) = -D \frac{\partial \bar{c}_v}{\partial z} \quad (15.41)$$

(The diffusivity of water vapor in air is about $2.4 \cdot 10^{-5} \text{ m}^2/\text{s}$ at 300 K.) Furthermore, the concentration of water vapor can be expressed in terms of the pressure of this component by using the ideal gas relation:

$$\bar{c}_v(z) = \frac{1}{RT_a} P_v(z) \quad (15.42)$$

For isothermal situations, the temperature is equal to the ambient temperature everywhere. If we introduce Equations (15.41) and (15.42) into Equ.(15.40) and integrate the first order differential equation from $z = 0$ to $z = d$, and remember that the current densities are constant, we obtain

$$I_{nv} = D \frac{P}{RT_a} \frac{A}{d} \ln \left(\frac{P - P_{va}}{P - P_g} \right) \quad (15.43)$$

A denotes the cross section of the container from which water evaporates, and P_{va} and P_g are the water vapor pressure in the air far from the container (given by its temperature and relative humidity) and the saturation vapor pressure at the same temperature, respectively.

Evaporation of hot water. Let us revisit the experiment described in Fig. 15.17. The water is hotter than the environment for most of the time, so we do not have isothermal conditions as assumed in the derivation performed above. If we assume the column of air above the water to be at T_a , and the water at T_w , we could apply Equ.(15.43) and get a simple result:

$$I_{nv} = D \frac{P}{RT_a} \frac{A}{d} \ln \left(\frac{P - P_{va}(T_a)}{P - P_g(T_w)} \right) \quad (15.44)$$

Interestingly, the pressure dependence of this expression fits data well, as shown by the solid line and the dots in Fig. 15.18. However, for an actual fit, the current in Equ.(15.44) has to be multiplied by a constant factor of the order of 10. While the form of Equ.(15.44) seems to apply to the evaporation of hot water from a container, the strength of the current is considerably larger than predicted by the simple model. Furthermore, experiments with different values of the depth of the water level do not show the dependence on d expected from Equ.(15.43) or (15.44). Vapor condenses on the inside of the glass container and evaporates again at different heights and joins the vapor coming from the surface of the body of water. This may explain the differences.

15.3.2 Evaporative Cooling

Evaporative cooling can be taken to mean two different things. On the one hand, bodies (solids, liquids) are cooled if a liquid at their surfaces evaporates. We have seen this effect several times already such as in the drop of temperature of a wet thermom-

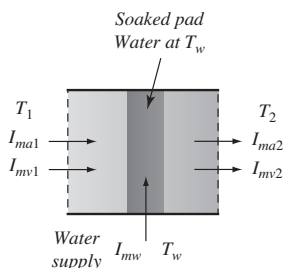


Figure 15.20: Relatively dry, hot air flows through a pad soaked with water. Because of evaporation, the temperature of the humid air exiting the duct is lowered, and its humidity is increased.

eter (Fig. 6.8). On the other hand, we may direct our attention to the air that is involved in evaporation and takes up vapor; its temperature is reduced. This plays a role in air-conditioning: in a hot and dry climate, we may want the comfort of cooler and more humid air. Below, two applications will be discussed: forcing dry air through a wet pad and the cooling of already cold water sitting in a container.

Dry air flowing through a wet pad. Consider a simple duct through which air can flow. The temperature of the air is to be lowered by evaporation of water in a pad through which the air is forced (Fig. 15.20). If we assume the system to be thermally insulated and if we can neglect mechanical and gravitational effects, the situation is similar to the one discussed in adiabatic saturation (Section 15.2.3) or to the case of mixing of streams of fluids (Section 8.6.4). For this reason, only the laws of balance will be formulated here.

There are three inflows and two outflows (Fig. 15.20). The steady-state balances of mass for air and water take the form

$$\begin{aligned} I_{ma1} &= I_{ma2} \\ I_{mv1} + I_{mw} &= I_{mv2} \end{aligned} \quad (15.45)$$

The law of balance of entropy contains six terms: one each for the incoming and outgoing substances and the production rate:

$$s_{a1}I_{ma1} + s_{v1}I_{mv1} + s_w I_{mw} + \Pi_S = s_{a2}I_{ma2} + s_{v2}I_{mv2} \quad (15.46)$$

The law of balance of energy only involves the convective currents of energy for the five currents in Fig. 15.20:

$$h_{a1}I_{ma1} + h_{v1}I_{mv1} + h_w I_{mw} = h_{a2}I_{ma2} + h_{v2}I_{mv2} \quad (15.47)$$

At both the inlet and the outlet, the currents of mass of vapor and air are related by the humidity ratios defined in Equ. (15.20). To complete a model, we need expressions for the entropies and enthalpies of air and water or steam for the conditions of temperature, pressure, and humidities that apply in the situation depicted in Fig. 15.20.

Evaporation of cold water. Water having the same temperature as the environment can still become colder by evaporation if it is inside a well insulated container that is open at the top. Historically, in dry climates, water was kept cool by storing it in amphoras which were sprayed with water, and fans were used to keep the air flowing over the wet containers.

Here is an experiment and dynamical model that shows how to deal with this situation. Water having roughly the temperature of the environment is poured into a relatively well insulated container that is open at the top. It is placed on an automatic scale, and water and air temperature, and relative humidity of the environment, are measured as functions of time (Fig. 15.21). We need to track the entropy and mass of the water and the entropy of the container in our model (it turns out that the dynamics of the container has to be taken into account if we want to get a good fit between model and data; see Fig. 15.21, center):

$$\begin{aligned} \dot{S}_w &= -I_{S, \text{evap}} - I_{S, \text{cond}} \\ \dot{m}_w &= -I_{m, \text{evap}} \end{aligned} \quad (15.48)$$

$$\dot{S}_c = -I_{S,ca} + I_{S,cond} \quad (15.49)$$

Note that, in principle, there should be a conductive entropy current going directly from the water to the air (or vice-versa); however, the simulation is not affected greatly by this addition.

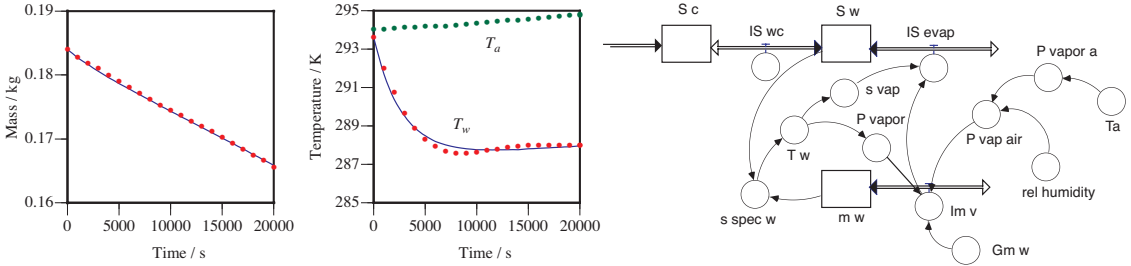


Figure 15.21: Evaporation of cold water in a relatively well insulated container that is open at the top. Mass (left) and water and air temperature (center) have been measured as functions of time (dots denote data). The relative humidity during the experiment was 0.15. Right: Diagram of a system dynamics model. Note that there is more to the model not shown here (top left of the diagram). Here, w, v, a, and c denote water, vapor, air, and container, respectively.

Constitutive laws have been assumed to be as follows. Since temperature differences are fairly small, entropy production due to conductive transfer has been neglected and transport models have been assumed to be linear. In particular, the flow of water evaporating from the surface of the water in the tank is modeled as in Equ.(15.36):

$$I_{m,v} = -G_{m,v} (\phi P_g(T_a) - P_g(T_w)) \quad (15.50)$$

The relation has been formulated for the flux of mass rather than for amount of substance. $G_{m,v}$ is a conductance for mass transfer. Conductive currents of entropy have been written accordingly. Note that the temperature of the water in the tank can be calculated on the basis of its specific entropy which equals the ratio of instantaneous values of entropy and mass. Together with expressions for vapor pressure and the specific entropy of vapor, the missing quantities can be calculated. Here is the relation for the evaporative current of entropy:

$$I_{S,evap} = s_{vap} I_{m,v} \quad (15.51)$$

where s_{vap} is the specific entropy of the steam leaving the surface of the body of water. The model performs quite well (see the solid lines in the diagrams on the left and at the center of Fig. 15.21).

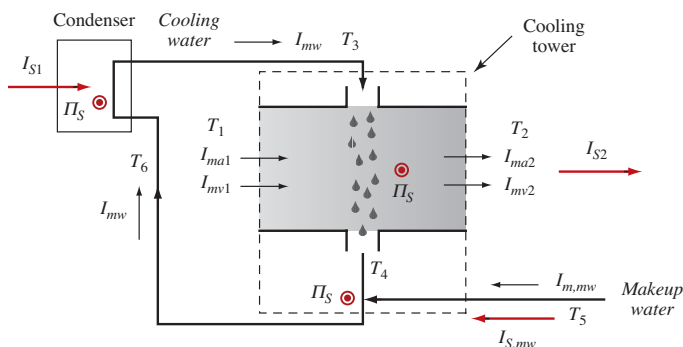
15.3.3 Cooling Towers

Consider cooling towers as a last application of evaporative cooling. Where the cooling needed for a large thermal power plant cannot be done by transferring the entropy to a river, a cooling tower may be used. Here, water used for the condenser of the plant is sprayed into a stream of relatively dry air so that a part of the water evaporates. The

portion of the cooling water that does not evaporate has given up entropy. Together with makeup water (used to replenish the flow of water through the condenser), the colder cooling water is returned to the condenser of the plant.

The processes going on can be envisioned in a schematic similar to the one showing evaporative cooling in Fig. 15.20. In place of the wet pad, we have cooling water falling through the stream of air forced through the device. (Naturally, the geometry of an actual cooling tower will be different from what we discuss here, but the processes can still be understood by the schematic shown in Fig. 15.22.)

Figure 15.22: Schematic of a cooling tower. The entropy that is rejected by the power plant (I_{S1}) has to be communicated to the environment.



Assume the power plant is designed to eject a current of entropy I_{S1} to the cooling water. At least this amount of entropy will have to be carried away by the moisturized air leaving the cooling tower.

We can calculate the performance of a cooling tower using the type of (steady-state) model discussed above and applied in Example 15.6 and Example 15.7. To exercise a less formal approach, consider the following simplified model that is suitable for estimates. The entropy coming from the power plant (I_{S1}) has to be communicated to the environment (I_{S2}). If we assume the entropy current leaving the cooling tower with the humid air to be equal to the one from the power plant, we neglect entropy production in the tower and the entropy current with makeup water. (Entropy production is mostly due to mixing of water, vapor, and air at different conditions, and the dissipation of the energy used for pumping, which is neglected here anyway.)

If we assume further that the temperature of the air flowing though the cooling tower does not change much, its entropy will not either. Therefore, all the entropy communicated to the tower from the power plant has to be in the water that is evaporated and added to the airflow:

$$I_{S2} = (s_{v2}\omega_2 - s_{v1}\omega_1)I_{ma} \quad (15.52)$$

This is so because ωI_{ma} is the current of water vapor in air if I_{ma} is the current of dry air (Equ.(15.20)). s_v denotes the specific entropy of vapor at its temperature and (partial) pressure. If we specify the condition of the air at the inlet and outlet of the cooling tower, we can calculate the humidity ratios according to what we have learned in the previous sections. Calculating the entropies poses a small problem. Equ.(15.52) shows that we cannot just work with the difference of the entropies at two states. To deal with this case properly, we have to make sure we have the entropy with respect to a well

defined state that holds for both points 1 and 2. This can be insured by setting the entropy of liquid water equal to zero at $T = 273 \text{ K}$ and $P = 101.3 \text{ kPa}$. The entropy of the vapor can be calculated from this if the entropy of vaporization and the temperature coefficient of enthalpy of the vapor are known (Example 15.9).

QUESTIONS

9. What kind of reasoning leads to the expression in Equ.(15.35)?
10. Why are the fluxes in the model of Fig. 15.19 spatially constant (independent of z)?
11. Why does the current of vapor in evaporation inside a container depend upon the ratio of the pressures of the dry air far from the water and near its surface?
12. If hot dry air is cooled by evaporating some water (as in Fig. 15.20), what happens to the exit temperature of the stream of air if the flow of water is increased? Do you expect there to be a minimum of entropy production for some water current, or does the entropy production rate vary monotonically?
13. Why is it possible to neglect entropy production in the model shown in Fig. 15.21
14. What are the conditions necessary for the entropy current leaving a cooling tower to be equal to the one rejected by the power plant? Where do you expect these conditions to be violated most strongly?

EXAMPLE 15.7. Cooling air by humidification.

Hot (40°C) dry ($\phi = 0.1$) air flows through an evaporative cooler as in Fig. 15.20. The current of mass of the air alone is 1.0 kg/s . How much water needs to be added each second to cool the air to 28°C ? (The water added has a temperature of 25°C) What will the relative humidity of the air at that point be? Ambient pressure is taken to be 1.0 atm .

SOLUTION: We formulate the laws of balance of energy and mass, the constitutive relations, and the properties of the substances in EES (Klein et al., 1991). The laws of balance take the forms

$$\begin{aligned} ha_{T1} \cdot I_{ma_1} + hg_{T1} \cdot I_{mv_1} + hw_{Tw} \cdot I_{mw_1} &= \\ ha_{T2} \cdot I_{ma_2} + hg_{T2} \cdot I_{mv_2} & \\ I_{ma_2} &= I_{ma_1} \\ I_{mv_2} &= I_{mv_1} + I_{mw_1} \end{aligned}$$

The constitutive relation needed are

$$\begin{aligned} Pv_{T1} &= \phi_1 \cdot Pg_{T1} \\ w_1 &= 0.622 \cdot Pv_{T1} / (P1 - Pv_{T1}) \\ I_{mv_1} &= w_1 \cdot I_{ma_1} \\ w_2 &= I_{mv_2} / I_{ma_2} \\ Pv_{T2} &= w_2 / (w_2 + 0.622) \cdot P1 \\ \phi_2 &= Pv_{T2} / Pg_{T2} \end{aligned}$$

and the pressures and enthalpies can be evaluated with the help of

$$\begin{aligned} Pg_{T1} &= \text{Pressure}(\text{Steam}, T=T1, X=1) & ha_{T1} &= \text{Enthalpy}(\text{Air}, T=T1) \\ hg_{T1} &= \text{Enthalpy}(\text{Steam}, T=T1, X=1) & ha_{T2} &= \text{Enthalpy}(\text{Air}, T=T2) \\ hg_{T2} &= \text{Enthalpy}(\text{Steam}, T=T2, X=1) & hw_{Tw} &= \text{Enthalpy}(\text{Steam}, T=Tw, X=0) \end{aligned}$$

$$P_{g_T2} = \text{Pressure}(\text{Steam}, T=T2, X=1)$$

If we now define the given quantities:

$$\begin{array}{lll} \phi_{1_1} = 0.1 & T1=40 & T_w = 25 \\ P1=101.3 & I_{ma_1} = 1 & T2 = 28 \end{array}$$

the model can be solved. It turns out that we need a current of water of 5.0 g/s to achieve the stated goal. The relative humidity of the cooler air will be 0.405.

EXAMPLE 15.8. Parameters for mass and entropy transfer in evaporative cooling of water.

Use the results of the experiment shown in Fig. 15.21 to estimate (a) the conductivity for mass for the evaporative process, and (b) the overall entropy conductivity of the container.

SOLUTION: (a) Consider the situation after $t = 15000$ s when the processes have almost reached steady-state conditions. The first diagram in Fig. 15.21 shows that the current of mass is almost constant at a value of roughly $(0.184 - 0.165) \text{ kg} / 20000 \text{ s} = 9.5 \cdot 10^{-7} \text{ kg/s}$. To determine the mass conductivity, we use Equ.(15.50)

$$G_{m,v} = - \frac{I_{m,v}}{\phi P_g(T_a) - P_g(T_w)} = - \frac{9.5 \cdot 10^{-7} \text{ kg}}{0.15 \cdot 2550 - 1700 \text{ s} \cdot \text{Pa}} = 7.2 \cdot 10^{-10} \frac{\text{kg}}{\text{s} \cdot \text{Pa}}$$

The humidity was 0.15, and the temperatures of air (21.5°C) and of water (15°C) were read from the diagram at the center of Fig. 15.21. Saturated vapor pressures were taken from Table 15.1.

(b) If we use the steady-state version of the law of balance of entropy for the water as expressed by the diagram on the right in Fig. 15.21, i.e.,

$$I_{S,cond} = I_{S,evap}$$

we can find the overall entropy conductivity from the water to the environment. We need to introduce constitutive relations in the law of balance:

$$G_S(T_a - T_w) = s_{vap}(T_w) I_{m,v}$$

which leads to

$$G_S = \frac{s_{vap}(T_w) I_{m,v}}{T_a - T_w} = \frac{8780 \cdot 9.5 \cdot 10^{-7} \text{ W}}{21.5 - 15 \text{ K}^2} = 1.3 \cdot 10^{-3} \frac{\text{W}}{\text{K}^2}$$

The specific entropy of the vapor has been taken from Table 15.1.

EXAMPLE 15.9. Estimating evaporation in a cooling tower.

Use the strongly simplified model of a cooling tower that led to Equ.(15.52) in order to find the flow of cooling water, the current of air and the amount of water evaporated for the following thermal power plant. Calculate the fraction of water that has to be resupplied (makeup water).

The plant has an electric power of 260 MW. The endoreversible part operates between 300°C and 40°C. The cooling water circulating through the tower arrives with a temperature of 40°C and returns to the condenser at 25°C. The temperature and humidity of the incoming air are 25°C and 20%, respectively; for the outgoing air they are 30°C and 90%.

SOLUTION: We first calculate the entropy current emitted by the (endoreversible part of the) engine. For a power of 240 MW and a temperature drop of 260 K, the current of entropy is

$$I_{S1} = \mathcal{P}/\Delta T = 260 \cdot 10^6 / 260 \text{ W/K} = 1.0 \cdot 10^6 \text{ W/K}$$

If we assume that the entropy can be communicated to the cooling water without dissipation, the current of cooling water is calculated from

$$I_{S1} = c_{pw} \ln(T_3/T_6) I_{mw}$$

$$I_{mw} = \frac{I_{S1}}{c_{pw} \ln(T_3/T_6)} = \frac{1.0 \cdot 10^6}{4200 \cdot \ln(313/298)} \frac{\text{kg}}{\text{s}} = 4850 \frac{\text{kg}}{\text{s}}$$

The state of the air at the inlet and outlet to the cooling tower allows us to calculate the vapor pressures:

$$P_{v1} = \phi_1 P_g(T_1) = 0.20 \cdot 3.17 \text{ kPa} = 0.634 \text{ kPa}$$

$$P_{v2} = \phi_2 P_g(T_2) = 0.90 \cdot 4.25 \text{ kPa} = 3.82 \text{ kPa}$$

Saturated vapor pressures have been taken from [Table 15.1](#). Now we estimate the (specific) entropy of vapor using the ideal gas model and the reference state T_{ref} , $P_{v,ref}$:

$$s_v(T, P_v) = s_{v,ref} + c_{pv} \ln\left(\frac{T}{T_{ref}}\right) - \frac{R}{M_0} \ln\left(\frac{P_v}{P_{v,ref}}\right)$$

Here, $c_{pv} = 1870 \text{ J/(K} \cdot \text{kg)}$ is the specific temperature coefficient of enthalpy of water vapor (it depends slightly upon temperature). $T_{ref} = 273$, and $s_{v,ref}$ and $P_{v,ref}$ are determined as follows. We set the entropy of liquid water equal to zero at 273 K. At this temperature, it takes about 9160 J/K of entropy to evaporate 1 kg of water which then ends up at a pressure of 0.61 kPa (see [Table 15.1](#)). Therefore,

$$s_{v,ref} = 9160 \text{ J/(K} \cdot \text{kg)} \quad , \quad T_{ref} = 273 \text{ K} \quad , \quad P_{v,ref} = 0.610 \text{ kPa}$$

This model yields pretty good results when compared to values found in [Table 15.1](#). Using this determination, the specific entropies at points 1 and 2 turn out to be equal to $s_{v1} = 9310 \text{ J/(K} \cdot \text{kg)}$ and $s_{v2} = 8510 \text{ J/(K} \cdot \text{kg)}$, respectively.

To find the current of mass of dry air necessary for making the operation of the cooling tower possible, we use Equ.(15.52) together with Equ.(15.21):

$$I_{S2} = 0.622 \left(s_{v2} \frac{P_{v2}}{P - P_{v2}} - s_{v1} \frac{P_{v1}}{P - P_{v1}} \right) I_{ma}$$

Setting $I_{S2} = I_{S1}$ and plugging in values yields a result of $I_{ma} = 5900 \text{ kg/s}$. This allows us to calculate the currents of water vapor at points 1 and 2 (23 kg/s and 143 kg/s) from which we find the rate at which water has to evaporate, namely, 120 kg/s. This equals 2.0% of the cooling water. [These estimates are pretty good. A model based on the balance of energy—which implicitly includes dissipation—using actual property values yields 5500 kg/s for the current of cooling water, and a rate of evaporation of 112 kg/s.]

15.4 VAPOR POWER AND REFRIGERATION CYCLES

In this last section of this chapter we will be dealing mostly with engineering applications of the thermodynamics of fluid systems, i.e., with vapor power cycles and refrigeration systems.²

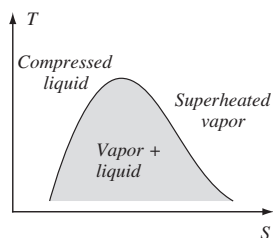


Figure 15.23: Compressed (sub-cooled) liquid, superheated steam, and mixtures of vapor and liquid are the main forms of a pure fluid.

15.4.1 Property Data and the Computation of Processes

If you want to calculate processes of simple fluids undergoing temperature and pressure changes, and phase changes and mixing, you will need detailed information about the properties of the substances involved. These properties are reported in the form of tables or graphs, of which the steam tables for water are the most famous. Even though you can also take advantage of computer programs providing the information in function format,³ it helps to look at the actual numbers when you learn about the subject. An overview of the three main segments of fluid states is shown in Fig. 15.23 (see also Fig. 15.5). Table 15.1 provides values for saturated water (liquid or vapor; mixtures are calculated from the values of the saturated fluids). Also, if you wish to be able to calculate changes in the region of the superheated vapor, appropriate tables have to be available (see Table 15.3 and Figures 15.28 and 15.29). Properties of subcooled or compressed liquid water complete the list of necessary materials (Fig. 15.25).

Saturated fluids. To orient ourselves to the properties of fluids, it is convenient to start with the state of saturation, since the *saturation line* naturally divides the domain of independent variables into the different sections discussed above. The transition from the liquid to the gaseous state of a fluid is outlined in the TS diagram. To catch this transition, one computes the values of thermodynamic properties of the saturated fluid, i.e., of saturated liquid and saturated vapor. We have seen what distinguishes the saturated fluid (and mixtures of the phases) from the rest: it is the nature of the chemical potential at those particular conditions. As we have learned during the description of phase changes, the chemical potential remains unchanged. Therefore, the potential is the same for both the liquid and the vapor at a given temperature.

The chemical potential of both phases is listed in the third column in Table 15.1. As you can show by directly calculating the potential using energy, volume, and entropy, its values are indeed equal for the liquid and the vapor:

$$u_l + Pv_l - Ts_l = u_g + Pv_g - Ts_g \quad (15.53)$$

Continuing with Table 15.1, the second column reports the vapor pressure of the fluid, while the last six columns list entropy, specific volume, and specific energy of both the liquid and the vapor. The values are given on a mass basis (specific values).

So far, we have used the TS diagram only for reporting fluid properties, but other diagrams are used as well. In Fig. 15.24, the distinctive saturation curve is presented for the refrigerant R123. The information is given in the TS and the pressure-enthalpy di-

2. For more information, see Moran and Shapiro (1992), or Cengel and Boles (2002).

3. See EES (Klein et al., 1991).

agrams. Depending on your purpose, you might use either diagram to discuss vapor processes.

Table 15.3: Properties of superheated water vapor^a

$T / ^\circ\text{C}$	0.3 bar			1.0 bar			3.0 bar		
	s	v	e	s	v	e	s	v	e
80	7.8282	5.4015	2483.8						
120	8.0358	6.0273	2542.4	7.4665	1.7931	2537.0			
160	8.2229	6.6485	2601.0	7.6591	1.9838	2597.5	7.1274	0.6506	2586.9
200	8.3944	7.2676	2660.1	7.8335	2.1723	2657.6	7.3108	0.7163	2650.2
240	8.5535	7.8855	2719.9	7.9942	2.3594	2718.1	7.4765	0.7804	2712.6
280	8.7021	8.5026	2780.7	8.1438	2.5458	2779.2	7.6292	0.8438	2775.0
320	8.842	9.1193	2842.3	8.2844	2.7317	2841.1	7.7716	0.9067	2837.8
360	8.9743	9.7356	2904.9	8.4171	2.9173	2904.0	7.9057	0.9692	2901.2
400	9.1001	10.3518	2968.5	8.5432	3.1027	2967.7	8.0327	1.0315	2965.4
440	9.2201	10.9677	3033.2	8.6634	3.2879	3032.5	8.1536	1.0937	3030.5
480	9.3349	11.5836	3098.9	8.7785	3.4730	3098.3	8.2692	1.1557	3096.6
520	9.4452	12.1994	3165.7	8.8889	3.6581	3165.2	8.3800	1.2177	3163.7

a. Units as in Table 15.1.

$T / ^\circ\text{C}$	10 bar			30 bar			100 bar		
	s	v	e	s	v	e	s	v	e
200	6.6932	0.2059	2621.5						
240	6.8805	0.2274	2692.2	6.2251	0.0682	2618.9			
280	7.0454	0.2479	2759.6	6.4445	0.0771	2709.0			
320	7.1954	0.2678	2825.6	6.6232	0.0850	2787.6	5.7093	0.0192	2588.2
360	7.3344	0.2873	2891.3	6.7794	0.0923	2861.3	6.0043	0.0233	2728.0
400	7.4648	0.3066	2957.2	6.9210	0.0994	2932.7	6.2114	0.0264	2832.0
440	7.5882	0.3257	3023.6	7.0521	0.1062	3003.0	6.3807	0.0291	2922.3
480	7.7055	0.3447	3090.6	7.1750	0.1129	3073.0	6.5287	0.0316	3005.8
520	7.8177	0.3635	3158.5	7.2913	0.1195	3143.2	6.6625	0.0339	3085.9
560	7.9254	0.3823	3227.2	7.4022	0.1260	3213.8	6.7862	0.0362	3164.0
600	8.0292	0.4011	3297.0	7.5084	0.1324	3285.0	6.9022	0.0384	3241.1
640	8.1293	0.4198	3367.7	7.6105	0.1388	3357.0	7.0119	0.0405	3317.9

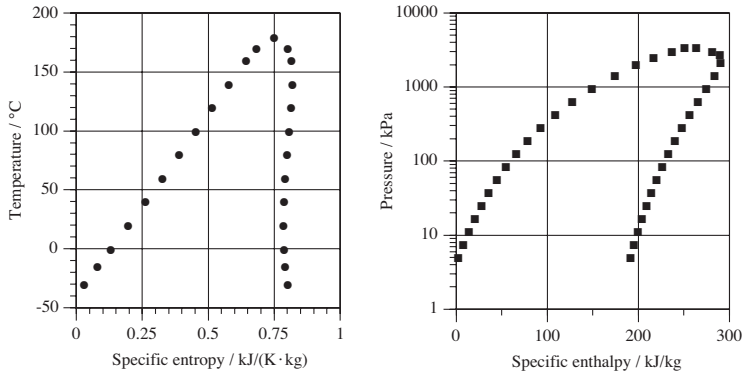
Subcooled (compressed) liquid. If a fluid exists in liquid form only, it may either satisfy the special condition of saturation (in which case its states would be found on the saturation line in Fig. 15.23), or it may be found in the subcooled (compressed) region. Since liquids are hard to compress, their condition usually does not deviate much

from that of the saturated liquid, if the pressure is not too high. Fig. 15.25 shows a small region of the TS diagram of water near the liquid saturation line. It demonstrates that, for a pressure of 300 bar, the temperature is larger by only about 5 K if the entropy is held constant. Put differently, for pressures in the range of up to a few hundred bar, the states lie in a narrow band around the saturation line. Entropy, energy, and volume of the liquid may be approximated by the saturated liquid data for the desired temperature, independently of pressure. Enthalpy, on the other hand, can be given by

$$h(T, P) = h_l(T) + (P - P_l)v(T) \quad (15.54)$$

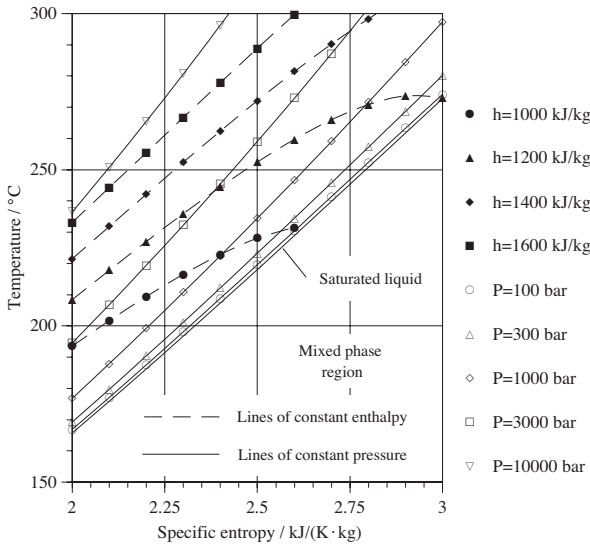
where the index l refers to the state of liquid saturation.

Figure 15.24: The saturation line for the refrigerant R123 looks quite different from that of water. While in the case of water, vapor will condense if it is compressed isentropically, this does not always happen with R123. (Consider, for example, a process starting with the saturated state at a temperature of 100°C, and leading to one at a lower temperature.) The curves have been computed using the program EES (Klein et al., 1991).



Note that, under these conditions, the lines of constant enthalpy are nearly horizontal, meaning that this quantity is constant for constant temperature. (We can draw the same

Figure 15.25: A small segment of the TS diagram of subcooled water. For pressures that are not too large, the state of water is well approximated by that of the saturated liquid. At very high pressures, deviations become increasingly important. The diagram shows lines of constant pressure and enthalpy. Computations were done using the program EES (Klein et al., 1991).



conclusion from the equation above for small specific volume and pressures that are not too large.) This is what we would expect of an incompressible substance. Take a closer look at the model of an *incompressible fluid*. Such a fluid is commonly defined as one having a constant specific volume, and whose energy depends only upon temperature. The enthalpy is then given by

$$h(T, P) = u(T) + Pv \quad (15.55)$$

Under these circumstances, the temperature coefficient of energy (the specific heat at constant volume) is a function of temperature only, and the temperature coefficient of enthalpy (i.e., the specific heat at constant pressure) must be equal to the former:

$$\begin{aligned} c_v(T) &\equiv \frac{\partial u(T)}{\partial T} = \frac{du}{dT} \\ c_p(T) &\equiv \frac{\partial h(T, P)}{\partial T} = \frac{du}{dT} \end{aligned} \quad (15.56)$$

Changes of energy and of enthalpy are obtained by integrating the appropriate expressions. For constant coefficients, the results take the form

$$\begin{aligned} u(T) &= u(T_0) + c(T - T_0) \\ h(T) &= h(T_0) + c(T - T_0) + (P - P_0)v \end{aligned} \quad (15.57)$$

The same arguments applied to the entropy of the incompressible fluid yield the result, which again holds for constant c :

$$s(T) = s(T_0) + c \ln\left(\frac{T}{T_0}\right) \quad (15.58)$$

These are all relations we have used before in applications. In summary, to compute property data for the compressed liquid, we may use data of the saturated liquid for a desired temperature, and adjust the enthalpy for pressure as in Equ.(15.54). Changes in temperature are taken into account according to the equations given above.

Mixtures of liquid and vapor: the quality. The conditions for which mixtures of a liquid and its vapor exist need special attention. It is customary to describe the properties in terms of the composition of the mixture, which is quantified by stating how much vapor is present relative to the total fluid:

$$x = \frac{n_g}{n_l + n_g} = \frac{m_g}{m_l + m_g} \quad (15.59)$$

This quantity is called the *quality* of the mixture (Fig. 15.26). Note that it is equivalent to the notion of the mole fraction (of vapor) of a two-component mixture. All the intermediate states of the mixed fluid (liquid plus vapor) can be computed on the basis of the values of the saturated fluid. This means that we do not need additional data for this set of conditions. A fluid with a quality of 0 or 1 simply corresponds to pure liquid or pure vapor, respectively. States with a quality between these values are found on the horizontal line in the TS diagram connecting the conditions of liquid and vapor. (See Fig. 15.27.)

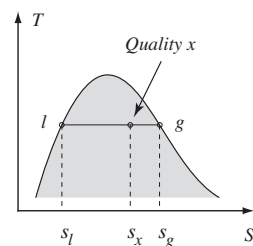
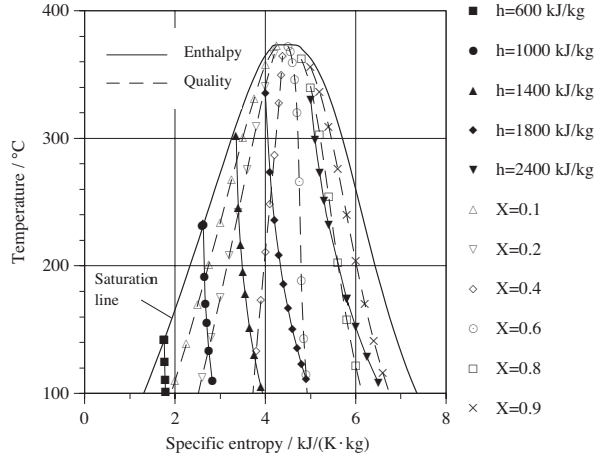


Figure 15.26: A state of quality x and the corresponding pure states (liquid and vapor).

Figure 15.27: Lines of constant enthalpy and of constant quality for the mixed phase states of water. Changes taking place at constant enthalpy include throttling processes (Section 8.6).



The total volume, entropy, energy, and enthalpy of the fluid mixture are expressed as the sum of the corresponding quantities for the liquid and the vapor. To start with the volume, the total specific volume is defined as the total volume divided by the total mass

$$\begin{aligned} v &= \frac{V}{m} = \frac{V_l + V_g}{m} = \frac{m_l v_l + m_g v_g}{m} \\ &= \frac{m_l}{m} v_l + \frac{m_g}{m} v_g \end{aligned}$$

which is equivalent to

$$v = (1 - x)v_l + xv_g \quad (15.60)$$

Exactly the same forms can be shown to apply to the other properties:

$$\begin{aligned} s &= (1 - x)s_l + xs_g \\ e &= (1 - x)e_l + xe_g \\ h &= (1 - x)h_l + xh_g \end{aligned} \quad (15.61)$$

Note that the values of s_l and s_g , for example, are those of the saturated states, which correspond to points on the saturation curve of Fig. 15.26. With this information, the values corresponding to any mixture of liquid and vapor can be computed.

Superheated vapor (steam). When we finally have pure vapor, the conditions of the fluid can be changed quite drastically with relatively modest changes of pressure and temperature. This is demonstrated in Fig. 15.28, which shows the part of the TS diagram of water to the right of the saturation line. The most important feature of the data presented in the figure is this: vapor can be treated as an ideal gas only if the pressure is not too high. The conditions for which the ideal gas model applies are marked by the horizontal sections of the lines of constant enthalpy. As you remember, this model requires the enthalpy of the fluid to be a function of temperature only. If the conditions

of the ideal gas are satisfied, we can apply all the simple relations derived in the previous sections and chapters. Fig. 15.29 indicates that water vapor contained in the atmosphere can be treated in this simple manner. This simplifies applications in atmospheric physics and air conditioning to a certain degree. In the realm of the “real” gases, however, detailed property data, again in the form of tables, graphs, or computer programs, have to be provided (Table 15.3). Calculations by hand are tedious but instructive, at least during the learning phase. Sketching processes in diagrams, however, always helps in visualizing the appropriate information.

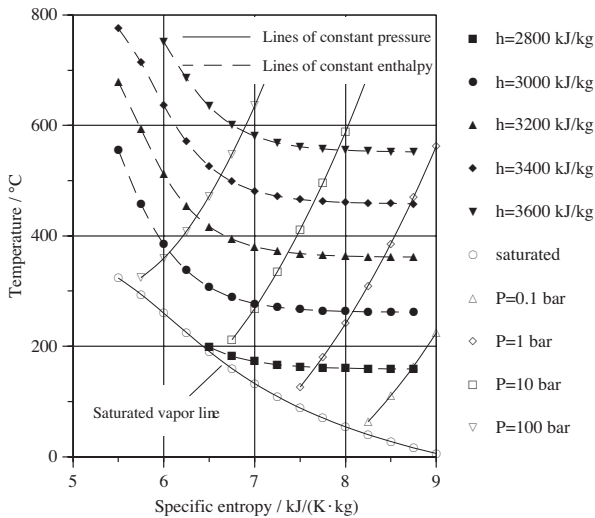


Figure 15.28: Superheated vapor region of the TS diagram provides data about the vapor state of the fluid. Lines of constant pressure and enthalpy are given. Where the lines of constant enthalpy are horizontal, we can consider the vapor to be in the ideal gas state. Computations were done using the program EES (Klein et al., 1991).

Calculating processes including phase transitions. Pure fluids that are allowed to go through phase changes play an important role in the sciences and in engineering. So far, we have a theory of uniform reversible processes, as discussed in the previous section. Even though real cases hardly ever conform to the conditions of this model,

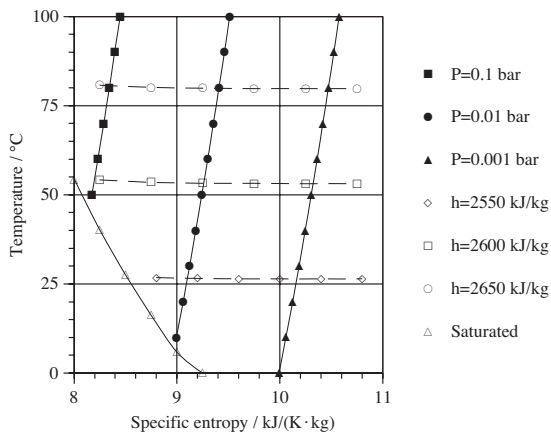


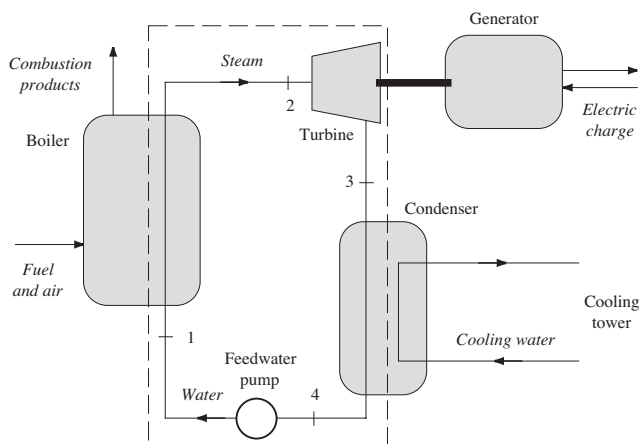
Figure 15.29: Superheated water vapor in the range interesting for moist air here on Earth. The ideal gas model may be applied to the computation of the properties of the water vapor contained in the air.

its results can still be applied. As long as we can provide information about the values of some variables at certain states, changes occurring between those states can be computed for the fluid even if irreversibilities are present. In the absence of more detailed information about actual processes, it is important to be able to approximate them by simple models. Experience shows that the results derived provide for a good basis from which to discuss of concrete cases in engineering and the sciences.

15.4.2 Vapor Power Cycles

Detailed fluid properties play an important role in the design of power plants which use vapor power cycles such as the steam power plant of Fig. 15.30. The thermal part of the plant consists of a boiler, turbine, condenser, and feedwater pump. A fluid such as water circulates through the boiler where steam is produced (points 1 to 2 in Fig. 15.30). Then the steam drives the turbine (points 2 to 3) and enters the condenser, where it is turned into liquid water (points 3 to 4). The feedwater pump increases the pressure of the fluid to the value at the inlet to the turbine (points 4 to 1), completing the cycle.

Figure 15.30: Steam power plant. Four devices operate on the water. The feedwater pump increases the pressure of the cold water. This water is then heated and evaporated in the boiler. Steam at high pressure drives the turbine and is thereby expanded adiabatically. Finally, the condenser turns the low pressure steam into water. The dashed line is the surface of the system that encloses the fluid operating in the power plant.



Principle of operation of a steam power plant. We can model the cycle undergone by the fluid as a sequence of steps that we have studied before. First consider each step to be reversible. Starting with the process in the boiler, liquid water at high pressure (P_1) is first heated and then evaporated; assume the step to be finished when all the water is turned into saturated vapor (point 2 in Fig. 15.31). We shall learn later about the consequences of superheating for the vapor power cycle. The step leading from point 1 to point 2 is supposed to take place at constant pressure ($P_2 = P_1$). A simplified model of what happens to the fluid expresses the energy current of heating in the boiler as follows:

$$|I_{E,12}| \approx \left(\frac{1}{2} (T_1 + T_2) (s_2 - s_1) + T_2 (s_2 - s_2') \right) I_m \quad (15.62)$$

I_m is the current of mass of the fluid flowing through the main loop of the power plant,

and T_1 can be approximated by T_4 . (The feedwater pump does not strongly increase the temperature of liquid water.) The upper and the lower temperatures of the cycle are determined by the pressure associated with the appropriate point. Alternatively, the first term in Equ.(15.62) can be computed using the enthalpy of the fluid.

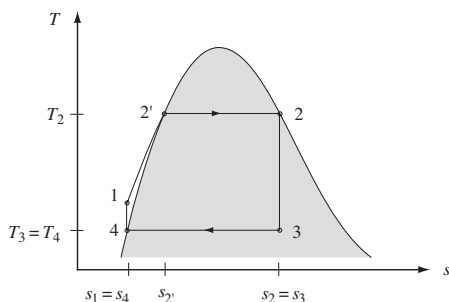


Figure 15.31: Vapor cycle undergone by an ideal fluid in a steam power plant. The sequence of steps is called the *ideal Rankine cycle*.

The second step of the cycle, from point 2 to point 3, is taken to be an isentropic (adiabatic and reversible) expansion of the fluid. According to Fig. 15.31, the quality of the steam leaving the turbine is less than 1, which means that droplets of water form in the turbine. This effect can easily lead to problems with operating the engine. Therefore one tries to keep the quality as high as possible, which can be achieved by superheating the steam (see below). The energy released in this step is transferred to the electric generator of the power plant; it can be calculated either directly or indirectly by calculating the other rates of energy transfer in the cycle.

The condenser, which is basically a heat exchanger operating at constant pressure, turns the steam which has not already condensed, into liquid water. Here, all the entropy added to the cycle in heating is removed and transferred to the environment through a cooling tower or similar device. The rate of energy transfer is easily calculated to be equal to

$$|I_{E,34}| = T_3(s_3 - s_4)I_m \quad (15.63)$$

The final step from point 4 back to point 1 consists of raising the pressure of the liquid to its upper value. The pump is supposed to operate reversibly and adiabatically. Since the density of the liquid usually does not change appreciably, the energy current necessary for operating the pump is computed as follows:

$$|I_{E,41}| \approx v_4(P_1 - P_4)I_m \quad (15.64)$$

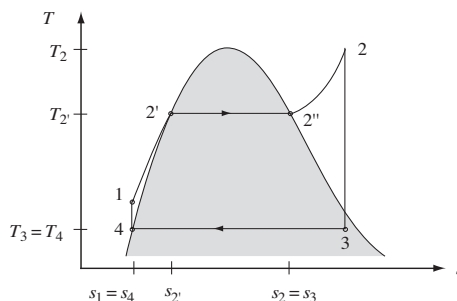
Overall, the current of energy delivered by the power plant is calculated from a steady state balance of energy for the system within the dashed line in Fig. 15.30:

$$\begin{aligned} |I_{E,23}| &= |I_{E,12}| - |I_{E,34}| - |I_{E,41}| \\ &\approx (h_2 - h_1 + T_2(s_2 - s_1) - T_3(s_3 - s_4) - v_4(P_1 - P_4))I_m \end{aligned} \quad (15.65)$$

Superheating in the power cycle. If heating of the fluid in the boiler is not stopped at the point where all the liquid has turned into saturated vapor, the cycle depicted in Fig. 15.31 changes as demonstrated in Fig. 15.32. The superheating is done in a heat

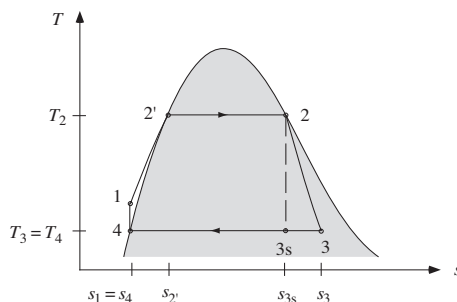
exchanger separate from the boiler, called the superheater. The boiler and superheater are known as the steam generator. Superheating has two main effects: first, the average temperature of heating of the fluid is higher than it would be without the additional process, leading to increased efficiency of the steam engine; second, the problem of low quality of the steam leaving the turbine is alleviated. You may even get pure vapor (quality equal to 1) at the exit of the turbine.

Figure 15.32: Vapor power cycle (ideal Rankine cycle) with superheating of the steam.



Irreversibilities in a vapor power plant. There are numerous sources of entropy production in a vapor power plant. If you look at Fig. 15.30, you can identify different processes leading to irreversibilities. First, there is the case of generation of heat that is normally accomplished by combustion. As you follow the path of entropy through the plant, you next have to consider the effect of the heat exchangers in the boiler and the condenser. In the fluid undergoing the Rankine cycle, entropy production chiefly occurs in the turbine and the pump, with the turbine usually contributing much more strongly. This latter effect is depicted in Fig. 15.33.

Figure 15.33: Entropy production in the vapor power cycle. The largest contribution to irreversibility in the fluid usually comes from the operation of the turbine.



It is important to consider the rates of entropy production in the entire plant if we wish to quantify the losses occurring as a result of irreversibility (Example 15.13).

15.4.3 Vapor Refrigeration and Heat Pump Systems

Refrigeration and the application of heat pumps to heating systems are two areas where intensive research and development are taking place. The common refrigerants used to date have to be replaced because they are responsible for reducing the ozone layer when released into the environment; and heat pumps have to compete with cheap

fossil fuel for a place in heating systems. Finally, in the future, we may wish to replace these sources of energy by those provided directly or indirectly by the Sun, again forcing us to adapt the technical systems.

A vapor Carnot refrigeration or heat pump cycle. We discussed the principle of operation of refrigerators or heat pumps in Chapter 4. There we saw that entropy is pumped from a lower temperature space, using supplied energy, to a higher temperature environment. A simple device for achieving this is a fluid running through a reverse Carnot cycle. If a substance is used which changes its phase in the range of temperatures and pressures encountered, the cycle may look like the one depicted in Fig. 15.34. Starting at point 1, the fluid which has just absorbed the entropy removed from the cold environment, is compressed isentropically to a state corresponding to point 2. Its temperature has therefore changed from the lower value, T_L , to the higher one, T_H . The fluid is then condensed at T_H to form a saturated liquid at state 3, rejecting the entropy it received during the step from point 4 to point 1. To ready the working fluid for picking up entropy again, its temperature must be reduced back to T_L which is achieved by an isentropic expansion to state 4. Finally, the fluid is evaporated while entropy is transferred into it from the cold space. This completes the cycle leading through points 1–2–3–4–1.

A technical realization of the Carnot cycle described uses four elements as shown in Fig. 15.35. We need a compressor to let the fluid undergo the step from point 1 to point 2. As in previous discussions, we first assume the process undergone by the fluid to be reversible; in other words, step 1–2 is a reversible adiabatic compression. Condensation of the high temperature and high entropy fluid takes place at constant pressure and temperature in the condenser, which is in contact with the high temperature environment. During step 2–3, the entropy picked up from the cold environment is rejected to the space at high temperature. The subsequent isentropic expansion requires a turbine which delivers useful energy for driving the compression. Finally, we need an evaporator in contact with the cold space.

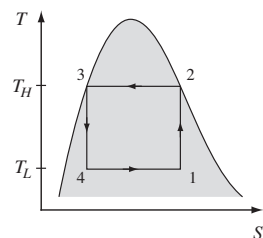
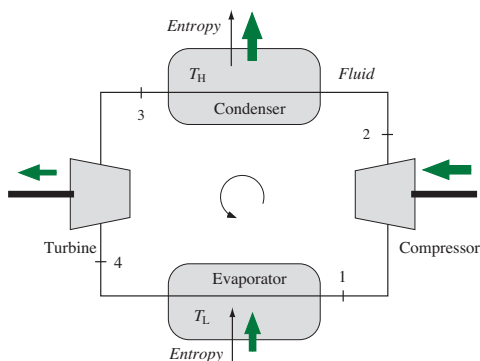


Figure 15.34: Carnot refrigeration cycle in the liquid-vapor region of a fluid. The cycle runs in the opposite direction from a Carnot power process.

Figure 15.35: Reversible four-step vapor refrigeration cycle requires four components. Evaporator and condenser are in contact with the cold and the warm spaces, respectively. Commonly, the turbine is replaced by a throttling valve as in Fig. 15.36.

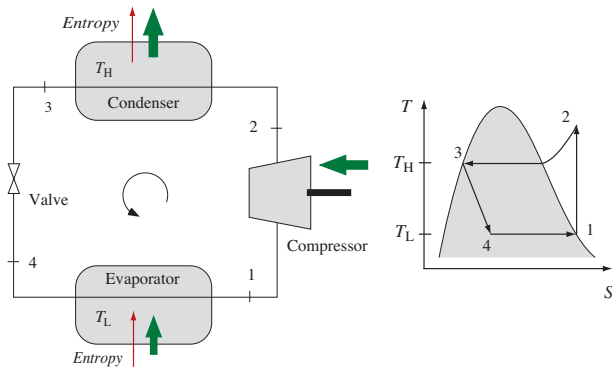
A more realistic vapor refrigeration cycle. Even if we could achieve this reversible operation of the Carnot cycle, we would still not realize it in practice for two reasons. First, since the fluid in state 1 is a mixture of liquid and vapor, the presence of liquid droplets might damage the compressor. Therefore, step 1–2 in Fig. 15.34 is replaced by one where we have only vapor (see Fig. 15.36). The latter process is called dry compression, in contrast to the wet compression discussed above.

Second, the turbine normally is left out of the cycle. First of all, step 3–4 delivers only a small amount of energy compared to the energy needed for compression. Additionally, turbines operate rather poorly under the conditions called for in a refrigeration cycle. Therefore, the turbine is replaced by a simple throttling valve; the liquid at point 3 is allowed to expand freely while conserving its specific enthalpy:

$$h_3 = h_4 \quad (15.66)$$

Naturally, this process is irreversible as is step 1–2, under realistic conditions in the compressor (not shown in Fig. 15.36).

Figure 15.36: A realistic vapor refrigeration cycle includes a throttling valve rather than a turbine for the expansion step. Also, step 1–2 is performed with vapor only, instead of with a mixture of vapor and liquid.



Absorption refrigeration. Energy is needed to raise entropy from a cold space to warmer surroundings. In the refrigeration cycles discussed, this energy is provided during the compression stage of the refrigerator or the heat pump. The compressor needs to be driven mechanically (or electrically) requiring other than thermal energy sources. There is a way, however, to use heat from a high temperature source to drive a refrigeration cycle.

Consider the setup as Fig. 15.37 which provides the technical means for an absorption refrigeration cycle. At point 1, a refrigerant, such as ammonia, leaves the evaporator as vapor. Next, the vapor enters the first of three elements which replace the compressor of a standard refrigerator. This device is an absorber, in which ammonia is absorbed by liquid water to form a strong water-ammonia solution. This step is exothermic, meaning that entropy will be rejected to the environment, requiring a means of cooling the absorber. The liquid solution then enters a pump which increases the pressure of the fluid to the level needed subsequently in the condenser. Since the fluid is a liquid, compressing it requires much less energy than has to be supplied in the compression step of a normal refrigerator. The strong solution leaves the pump at high pressure and enters a generator where a high-temperature source of entropy drives the ammonia out of the solution.

Now the process splits into two paths. The weak solution (essentially water obtained after the ammonia has been driven out) returns to the absorber through a valve which allows for the pressure of the fluid to be reduced to its value in the lower portion of the cycle. Ammonia vapor at high pressure and temperature, on the other hand, enters the condenser, where the entropy picked up from the space to be cooled is rejected to the environment. The vapor finishes its cycle by passing through the throttling valve

from point 3 to point 4, and by subsequently flowing through the evaporator where it again absorbs entropy.

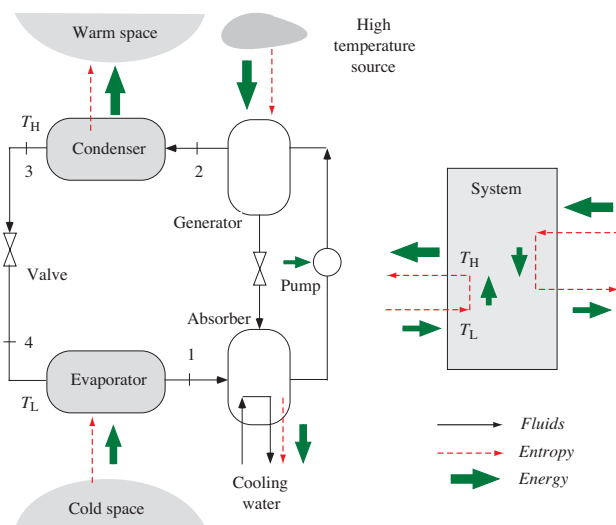


Figure 15.37: In an absorption refrigeration or heat pump system, the energy needed to pump entropy from a cold to a warm space is provided by a thermal process running between a generator and an absorber. In the absorber, the fluid of the refrigeration cycle (ammonia) is absorbed by a liquid (water). In the generator, heat from a high temperature source drives the refrigerant out of the strong solution. The former step is exothermic, while the latter is endothermic. (See also Herrmann, 2009.)

If you consider the thermodynamics of this entire process, you will notice that the energy needed to pump entropy from the cold space to the warmer surroundings is provided by lowering entropy from the high temperature source through the generator to the absorber and into the fluid used to cool the latter device. In effect, we have a “thermal transformer” in analogy to electrical or mechanical transformers (a gear box would provide an example of the latter). The flow diagram in Fig. 15.37 provides an explanation of the process.

Having a means of pumping heat without the need for electrical power allows for refrigeration and heat pump processes to be directly driven by the Sun. Absorption refrigeration has been studied extensively in solar energy engineering. The solar collectors, absorber, pump, and generator, however, may increase the cost of such systems considerably, making them too expensive where electrical power is cheap.

QUESTIONS

15. How are properties of mixtures of liquid and vapor calculated?
16. What is the meaning of the saturation line?
17. Consider an amount of liquid being converted into steam. What can be said about the chemical potential of the mixture of liquid and steam along the horizontal line in 15.26?
18. What does Equ.(15.54) tell us about the chemical potential of a compressed liquid at different pressures for a given temperature?
19. Why is the temperature coefficient of enthalpy of an incompressible fluid equal to the temperature coefficient of energy?
20. What problem can occur in a turbine if the steam flowing in is saturated?
21. Why does step 3-4 in Fig. 15.36 run to the lower right in the TS diagram?

EXAMPLE 15.10. The entropy of a mixture of water and water vapor.

Water is found to vaporize at a temperature of 200°C. If there are 12 kg of liquid water and 18 kg of water vapor present, how large is the entropy of the mixture? Estimate the necessary values from Fig. 15.27.

SOLUTION: First, we determine the quality of the mixture of steam and water. It is given by

$$x = \frac{m_{\text{vapor}}}{m_{\text{liquid}} + m_{\text{vapor}}} = \frac{18}{12 + 18} = 0.60$$

Now we need only the specific entropies of saturated water and of saturated steam at a transitional temperature of 200°C. According to Fig. 15.27, the values are 2300 J/(K·kg) and 6400 J/(K·kg), respectively. Using Equation (201a), we calculate the specific entropy of the mixture to be equal to

$$s = (1 - x)s_{\text{liquid}} + xs_{\text{vapor}} = (1 - 0.6) \cdot 2300 + 0.6 \cdot 6400 = 4760 \frac{\text{J}}{\text{K} \cdot \text{kg}}$$

With a total mass of 30 kg, the final result is 143 kJ/K.

EXAMPLE 15.11. Energy currents and efficiency of an ideal Rankine cycle.

An ideal Rankine cycle is operated for water at a high pressure of 80 bar and a low pressure of 0.1 bar. Steam is not superheated. (a) With a current of water of 100 kg/s, estimate the energy current with respect to the fluid in the boiler; use the diagrams showing fluid properties provided in this chapter. (b) How large is the energy current leaving the power plant due to cooling? (c) What is the power necessary to operate the feedwater pump? (d) Calculate the thermal efficiency of the cycle. (e) If the water used for cooling the plant enters at a temperature of 20°C and leaves at 35°C, how large does the current of mass of the cooling liquid have to be? (f) Calculate the quality of the fluid after isentropic expansion. (g) If the quality at the end of isotropic expansion is equal to 1, what is the efficiency of the cycle?

SOLUTION: Since you will probably solve the problem by reading property values from the graphs, you will get only approximate results. (Try solving this same problem with values read from tables or computed using appropriate programs.) First consider Fig. 15.4, which has been redrawn in a slightly different manner in Fig. 15.33 and Fig. Ex.11. Both cycles, i.e., those with and without superheating, have been superimposed on the graph below. The former joins the points 1 – 2' – 2'' – 3' – 4 – 1, while the latter includes point 2 and 3.

The lines of constant pressure for 0.1 bar, 60 bar, and 150 bar have been included. For the upper pressure of 100 bar, we have to interpolate in the diagram. We can read the following values from this graph and from Figures 15.10 and 15.27 (see Table 15.4 below):

(a) The energy current added to the steam in heating from point 1 to point 2'' can be estimated as in Equ.(15.62):

$$\begin{aligned} I_{E,1-2''} &= \left[T_{m,1-2'}(s_{l,2''} - s_{l,1}) + T_H(s_{g,2''} - s_{l,2'}) \right] I_m \\ &= [450 \cdot (3.2 - 0.7) + 573 \cdot (5.7 - 3.2)] \cdot 100 \text{ kW} = 255 \text{ MW} \end{aligned}$$

(b) Condensation takes place at constant temperature from point 3' to point 4:

$$I_{E,3'-4} = T_l(s_{g,2''} - s_{l,1}) I_m = 323 \cdot (5.7 - 0.7) \cdot 100 \text{ kW} = 162 \text{ MW}$$

(c) The energy current necessary for compressing the liquid from the state at point 4 to the one

at point 1 turns out to be rather small:

$$I_{E,4-1} \approx v(P_1 - P_4)I_m \approx 1.2 \cdot 10^{-3} \cdot 8 \cdot 10^6 \cdot 100 \text{ W} = 1 \text{ MW}$$

Table 15.4: Steam properties at low and high pressure in the cycle

Pressure	$T_{\text{evaporation}}$	s_l	s_g
0.1 bar	50°C	0.7 kJ/(K·kg)	
80 bar	300°C	3.2 kJ/(K·kg)	5.7 kJ/(K·kg)

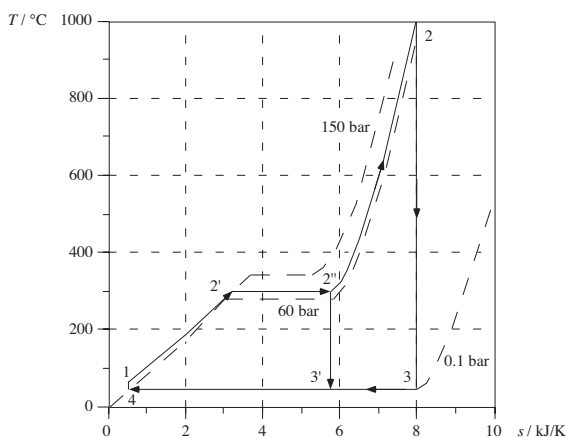


Figure Ex.11

(d) The numbers computed so far let us calculate the thermal efficiency of the plant:

$$\eta = \frac{(I_{E,1-2''} + I_{E,4-1}) - I_{E,3'-4}}{I_{E,1-2''} + I_{E,4-1}} = \frac{256 - 162}{256} = 0.37$$

(e) The entire energy current discharged in the condenser must be carried away by the cooling water. For this fluid, we can assume conditions of constant pressure and constant temperature coefficient of enthalpy. Therefore we have

$$c_p I_{m, \text{cooling}} (T_{c,H} - T_{c,L}) = I_{E,3'-4} \Rightarrow I_{m, \text{cooling}} = 2570 \text{ kg/s}$$

(f) By extrapolating the lines of constant quality in Fig. 15.27 down to a temperature of 50°C, we obtain a value of $x = 0.7$ for the quality of the vapor at point 3'.

(g) To answer this question, we have to recalculate the quantities obtained above, this time including superheating of the steam from point 2" to point 2. The important quantity to be read from the graph is the specific entropy of 8.0 kJ/(K·kg) at a temperature of about 1000°C at point 2. Estimates of the additional or new energy currents are

$$I_{E,2'-2} = T_{m,2'-2} (s_{g,2'} - s_{g,2}) I_m = 923 \cdot (8.0 - 5.7) \cdot 100 \text{ kW} = 210 \text{ MW}$$

$$I_{E,3'-4} = T_l (s_{g,2'} - s_{l,1}) I_m = 323 \cdot (8.0 - 0.7) \cdot 100 \text{ kW} = 236 \text{ MW}$$

The new thermal efficiency turns out to be $((256+210)-236)/(256+210) = 0.49$.

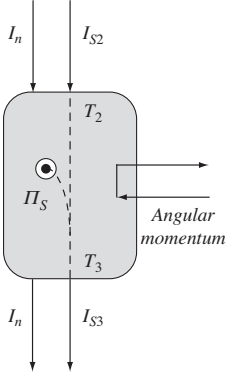
EXAMPLE 15.12. Entropy production and efficiency of a turbine.


Figure Ex.12

The isentropic efficiency of a turbine is defined as the ratio of its actual power and the power it would have if it were operated isentropically. (a) Draw a flow diagram for the operation of the turbine. (b) Derive an expression for the rate of entropy production of the turbine in terms of the efficiency, the enthalpies of the fluid at points 2 and 3s in Fig. 15.33, and the current of mass of the fluid.

SOLUTION: (a) According to the discussion of flow processes in Chapter 8, the flow diagram including the effect of irreversibility must look as shown in Fig. Ex.12. While the current of amount of substance is constant, the flux of entropy increases because of irreversibility.

(b) The energy current associated with the mechanical process of the turbine can be calculated as the difference of the energy fluxes entering and leaving the system together with the steam. According to Section 8.3, the latter currents can be written in terms of the flux of amount of substance, the chemical potentials, and the molar entropies:

$$\begin{aligned} |I_{E, mech}| &= |I_n| \left[(\mu_2 + T_2 \bar{s}_2) - (\mu_3 + T_3 \bar{s}_3) \right] = |I_n| \left[(\mu_2 + T_2 \bar{s}_2) - \left(\mu_3 + T_3 \left(\bar{s}_2 + \frac{1}{I_n} \Pi_S \right) \right) \right] \\ &= |I_n| \left[(\mu_2 + T_2 \bar{s}_2) - (\mu_3 + T_3 \bar{s}_2) \right] - T_3 \Pi_S \end{aligned}$$

The term multiplying the current I_n is equal to the difference of the molar enthalpies of the fluid at points 2 and 3s in Fig. 15.33. Therefore we have

$$\begin{aligned} |I_{E, mech}| &= |I_n| \left[\bar{h}_2 - \bar{h}_{3s} \right] - T_3 \Pi_S \\ &= |I_m| \left[h_2 - h_{3s} \right] - T_3 \Pi_S \end{aligned}$$

While the quantity on the left-hand side is the real power of the turbine, the first term on the right is the isentropic power. With the definition

$$\eta_{turbine} = |I_{E, mech}| / |I_{E, mech}|_S$$

we can express the rate of production of entropy as follows:

$$\begin{aligned} T_3 \Pi_S &= |I_{E, mech}|_S - |I_{E, mech}| = |I_{E, mech}|_S - \eta_{turbine} |I_{E, mech}|_S \\ &= (1 - \eta_{turbine}) |I_m| \left[h_2 - h_{3s} \right] \end{aligned}$$

EXAMPLE 15.13. Contributions to irreversibility in a steam power plant.

Consider a power plant running a vapor cycle as described in Example 15.11 (without superheating). Allow for the adiabatic expansion in the turbine to be irreversible. Additional information is provided about the situation in the heat exchangers and in the burner. Calculate the relative importance of the different sources of irreversibility. (a) Assume that methane is burned as fuel using the theoretical amount of air. The hot gases are cooled to 500°C in the heat exchanger, where steam is produced, before they are emitted through the stack of the power plant. Calculate the flux of mass of methane and air necessary to operate the cycle. Calculate the rates of production of entropy for the combustion and for heat transfer in the heat exchanger. (b) Let the turbine have an isentropic efficiency of 90%. Calculate the rate of entropy production in the turbine. (c) What is the rate of entropy production in the heat exchanger where the steam is condensed? (d) Express each contribution to the rate of production of entropy as a fraction of the total irreversibility.

SOLUTION: There are four sources of irreversibility to be considered (the contribution to the production of entropy in the pump is neglected). The schematic of the plant shows the corresponding four control volumes.

(a) Burning of methane with air was discussed in Example 8.11. In the accompanying diagram, the flame temperature and the rate of entropy production per mole of methane burned in unit time can be found.

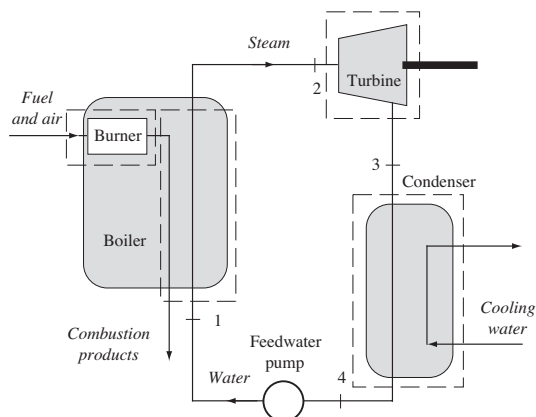


Figure Ex.13.1

The energy current $I_{E,1-2''}$ was calculated in Example 15.11 as 255 MW. Now, two expressions for the balance of energy for both the burner and the heat exchanger, and for the heat exchanger alone, can be established:

$$I_{E,1-2''} = I_n \left[(\bar{h}_{\text{CH}_4} + 2\bar{h}_{\text{O}_2} + 3.76 \cdot 2\bar{h}_{\text{N}_2})_{T_a} - (\bar{h}_{\text{CO}_2} + 2\bar{h}_{\text{H}_2\text{O}} + 3.76 \cdot 2\bar{h}_{\text{N}_2})_{T_{\text{ex}}} \right]$$

$$I_{E,1-2''} = I_n \left[(\bar{h}_{\text{CO}_2} + 2\bar{h}_{\text{H}_2\text{O}} + 3.76 \cdot 2\bar{h}_{\text{N}_2})_{T_{\text{flame}}} - (\bar{h}_{\text{CO}_2} + 2\bar{h}_{\text{H}_2\text{O}} + 3.76 \cdot 2\bar{h}_{\text{N}_2})_{T_{\text{ex}}} \right]$$

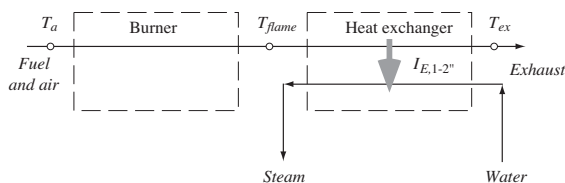


Figure Ex.13.2

I_n is the flux of amount of substance for methane, and T_{ex} denotes the temperature of the exhaust gases. T_a is set equal to 298 K. With $T_{\text{flame}} = 2330$ K and $T_{\text{ex}} = 773$ K, the flux of amount of substance of methane turns out to be 400 mole/s, which translates into a mass flux of 6.4 kg/s for methane and 110 kg/s for air. Now, with the results of Example 8.11, the rate of production of entropy in the burner must be equal to

$$\Pi_S = 763 \frac{\text{W}}{\text{K} \cdot (\text{mole} \cdot \text{s}^{-1})} \cdot 400 \frac{\text{mole}}{\text{s}} = 3.05 \cdot 10^5 \text{ W / K}$$

The balance of entropy for the heat exchanger, on the other hand, takes the form

$$\begin{aligned} \Pi_S &= I_{m, steam}(s_2'' - s_1) \\ &\quad - I_{n, CH_4} \left[(\bar{s}_{CO_2} + 2\bar{s}_{H_2O} + 3.76 \cdot 2\bar{s}_{N_2})_{T_{flame}} - (\bar{s}_{CO_2} + 2\bar{s}_{H_2O} + 3.76 \cdot 2\bar{s}_{N_2})_{T_{ex}} \right] \end{aligned}$$

or

$$\begin{aligned} \Pi_S &= 100 \frac{\text{kg}}{\text{s}} (5700 - 700) \frac{\text{J}}{\text{K} \cdot \text{kg}} - 400 \frac{\text{mole}}{\text{s}} (2.80 \cdot 10^3 - 2.35 \cdot 10^3) \frac{\text{J}}{\text{K} \cdot \text{mole}} \\ &= 3.20 \cdot 10^5 \text{ W / K} \end{aligned}$$

(b) The rate of entropy production in the turbine can be calculated according to the results of Example 15.12. The numbers computed in Example 15.11 tell us that the isentropic power of the turbine is 256 MW – 162 MW = 94 MW. Therefore, the rate of entropy production is

$$\Pi_S = \frac{1}{T_L} (1 - \eta_{turbine}) I_{E, 2 \rightarrow 3} = \frac{1}{323} (1 - 0.90) \cdot 94 \cdot 10^6 \text{ W / K} = 0.29 \cdot 10^5 \text{ W / K}$$

(c) We have to recalculate the specific entropy of the steam leaving the turbine and entering the condenser. This is done simply by adding the entropy produced in the turbine to the value at point 2 in the power plant. With $s_3 = s_2' + 0.29 \text{ kJ/(K} \cdot \text{kg)} = 6.0 \text{ J/(K} \cdot \text{kg)}$, the balance of entropy for the condenser is given by

$$\begin{aligned} \Pi_S &= -I_{m, steam}(s_3 - s_1) + I_{m, cooling} C_{p, water} \ln \left(\frac{T_{c, out}}{T_{c, in}} \right) \\ &= -100 \cdot (6000 - 700) \text{ W / K} + 2720 \cdot 4200 \cdot \ln \left(\frac{308}{293} \right) \text{ W / K} = 0.40 \cdot 10^5 \text{ W / K} \end{aligned}$$

The mass flux of the cooling water has to be recalculated as well; its new value is 2720 kg/s.

(d) Relative contributions to irreversibility and fluxes of entropy with respect to the entire plant appear in [Table 15.5](#).

Table 15.5: Irreversibilities in a power plant

Contribution	Fraction of total
Entropy production as a result of combustion	0.44
Entropy production in boiler heat exchanger	0.46
Entropy production in turbine	0.04
Entropy production in condenser heat exchanger	0.06
Entropy flux with fuel and exhaust	0.18
Entropy flux to environment through condenser	0.82

EXERCISES AND PROBLEMS

1. Prove that the density of moist air is always smaller than that of dry air at the same temperature and pressure.
2. During the day, at a temperature of 30°C, the relative humidity of the air was measured to be 60%. How far does the temperature have to drop at night for dew to form on the grass?
3. Show that the humidity ratio given in terms of the wet bulb temperature by Equ.(15.33) can

be approximated as follows:

$$(\omega' - \omega_1) \Delta h_v = c_{Pa} (T_a - T_{wb})$$

$$\omega' = 0.622 P_g (T_{wb}) / P$$

What approximations have to be made? Give an interpretation of the first of these equations.

4. Show that the expression for the total flux of water vapor in a column of (still) humid air above a body of water is given by Equ.(15.40).
5. Derive the differential equation for diffusion of water vapor in a container as in Fig. 15.19, and show that its solution is given by Equ.(15.43).
6. A stainless steel temperature probe is placed in water and then removed with a drop of water hanging from its end. Data can be found in Equ.(6.8). Create a simple system dynamics model that might explain this phenomenon. What parameters need to be known if we wish to use the model to determine the current of water from the drop due to evaporation?
7. The Rankine-Process is a model for the processes undergone by the working fluid (water and steam) in a power plant with a steam turbine (solid line in the diagram). From 1 to 2, the water is warmed by heating. At the same time, the pressure is raised to 60 bar. Further heating leads to total evaporation (2 to 3). Then, at constant pressure, the steam is further heated (3 to 4). Between 4 and 5, the steam is expanded isentropically in the turbine (the pressure here reduces to 1 bar). Then the steam is condensed in a cooler (5 until 1). In the following, consider 1 kg of water.

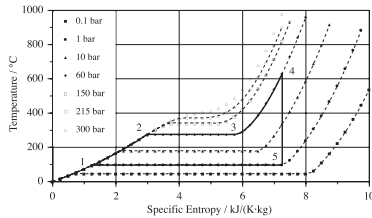


Figure P.7

(a) Treat the steam from point 3 to 4 as an ideal gas with a temperature coefficient of enthalpy (specific heat at constant pressure) of 3000 J/(K·kg). How much entropy must be introduced to the gas so that its temperature increases as seen in the diagram? Compare your theoretical calculation with the diagram. (b) How much energy is released in the cooler into the environment per kilogram of water? (The process from point 5 to 1). What is the flow of energy to the environment when the mass flow of the working fluids through the plant is 800 kg/s?

8. Determine the vapor pressure of Refrigerant 123 (R123) as a function of temperature. It is known that at 0°C the vapor pressure is 32.7 kPa. Use data from Fig. 15.24 and compare your result to Fig. P.8.
9. Express the efficiency of the ideal Rankine cycle in terms of the average temperature of heating. Neglect the feed-water pump.
10. Discuss the effect of changing the upper and the lower operating pressures of the Rankine cycle. Why is a condenser used in vapor power plants if steam leaving the turbine could be discharged directly to the environment?
11. Calculate the Carnot efficiency of the cycles running between the upper and the lower operating temperatures occurring in the processes of Example 15.11 (300°C and 40°C, without superheating). Does the difference between the Carnot efficiencies and the values calculated in that example result from dissipation?

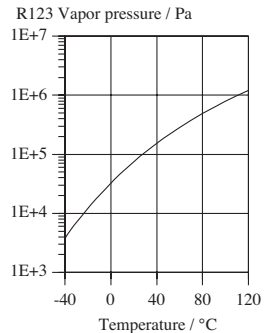


Figure P.8

12. Assume the furnace of the Carnot cycle proposed in Problem 11 to operate at 500°C and the condenser at 20°C , respectively. The cycle undergone by the working fluid is supposed to be the same as before. Calculate the rate of production of entropy and the rate of loss of availability.
13. (a) Estimate the efficiency of a vapor power cycle without superheating designed for the fluid R123. The heat is supposed to be delivered by solar collectors such as vacuum tubes. Saturated liquid enters the evaporator at a pressure of 8.0 bar, while the condenser operates at a temperature of 30°C . (Use property data found in [Fig. 15.24](#) and [Fig. P.8.](#)) (b) If the collectors deliver an energy current of 350 W per square meter of collector area, what is the minimum collector area needed per kW of power of the engine?
14. Estimate the amount of entropy produced in the throttling process of a refrigerant if the following data are given: the initial and the final pressure, and the initial and the final specific volume of the fluid.
15. Superheated water vapor at a pressure of 30 bar and a temperature of 300°C expands isentropically to a state with a temperature of 100°C . (Such a change might occur for adiabatic expansion of an ideal fluid in a turbine.) (a) Calculate the specific entropy and enthalpy of the fluid. (b) Determine the pressure and the temperature at which the fluid begins to condense. (c) Calculate the pressure and the quality of the fluid mixture at the final state. Perform the calculations by interpolation of the graphs provided above.
16. Superheated water vapor at a pressure of 10 bar and a temperature of 400°C is expanded in an isobaric process until the state of saturated liquid is reached. (a) How much entropy must be emitted or absorbed by 10 kg of the fluid? (b) How much energy is transferred in heating or in cooling? (c) How much energy has been transferred as a consequence of the mechanical process? Use tables provided in this chapter for calculations.